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CATALYTIC CHEMISTRY

by

HENRY WILLIAM LOHSE, Ph.D., F.C.I.C.

Consulting Chemist

1945

CHEMICAL PUBLISHING CO., INC.

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FOREWORD

A BOOK, Sabatier's Catalysis in Organic Chemistry, was a powerful catalyst in the study of catalysis. Many catalytic phenomena had been known for a long time. The word catalysis was coined by Berzelius a century ago. In the pre-Sabatier period, the finding of a case of catalysis was news. Now discovering a reaction that is non-catalytic would be news—interesting, if true. Perhaps most, if not all, of the chemical reactions, with which we are acquainted, go the way they do on account of catalysts, the presence of which we do not suspect. Of the innumerable thermodynamically possible reactions which we can write, probably a large proportion can be made to go by finding the "suitable catalyst" or eliminating anti-catalysts.

The more we study chemical reactions the more we are impressed with the importance of small amounts of so-called impurities, traces of water, peroxides, alkali, iron, copper and other substances which may be present. The catalytic effect of copper has been found to be a far more sensitive test for its presence than any analytical reaction. In the study of trace elements, in nutrition, the limitation has been the difficulty of finding foods sufficiently free of the elements in question to serve as blanks. Dr. Lohse, who has had long experience in spectroscopic analysis, lays great stress on the possible importance of the traces of other metals in the silver, copper, iron and nickel which we call the catalysts. Much has been discovered as to the effects of "promoters" which are intentionally added to catalysts. What about things that are already there?

Sabatier covered the field of organic catalysis; no mortal can do that now. Dr. Lohse has brought together many facts, but his chief concern has been the significance of their relations. May this book catalyze further progress in catalysis!

E. EMMET REID

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AUTHOR'S PREFACE

In writing this book, I have aimed at a brief factual presentation of the underlying principles of catalytic phenomena and the application of catalytic reactions in industrial processing. In many cases, no attempt has been made to modify the original author's view, although such a presentation may lack cohesion. This is meant to reflect the multiplicity of experience and also the variance in conceptions which exist in catalytic chemistry up to this time. Also, I do not honestly feel that, up to this time, enough attention has been paid to the presence of impurities in catalytic reaction systems, nor has complete enough account been given of the various substances present in the reaction systems during the reactions, to warrant sweeping statements even when based on a very large number of reports on catalytic research. Furthermore, it must be kept in mind that catalytic reactions are extremely varied, and the data obtained in catalytic work are very often influenced by the history of the case at hand.

No claim is made of an exhaustive presentation of references, and references have often been left out with much regret due to the limits of space. The tendency has been to include as much as possible, but with all the references included, the text is already heavy, and for that reason some very good references have been omitted. It can, of course, be disputed to what extent references should be included or left out; but it has been my aim to present a text which, when carefully studied, will permit a chemist with elementary training to obtain a concrete idea what catalytic chemistry deals with and what its working principles are. Numerous references have been made to original treatises on specialized subjects which, it is hoped, will be helpful to those who want to study any specific subject. Undoubtedly, a text such as this can be improved by constructive criticism, and it will be a pleasure to receive suggestions from the readers.

Considerable stress has been laid on the subject of minor constituents (impurities) but, unfortunately, there are very few published data which can be included at this time. This subject deserves considerable attention and future specific research.

I wish to thank most heartily those who have assisted in reading the manuscript before going to the printer and for the many valuable criticisms and suggestions received.

First of all, acknowledgment and many thanks are due to Dr. E. Emmet Reid, Professor Emeritus, Johns Hopkins University, for reading, correcting and criticising the manuscript to page 360 (Production of Motor Fuels). Professor Emmet Reid's experienced criticism was of much assistance, and those of his original suggestions which are cited are followed with the affix E.E.R. in parentheses. Professor, Dr. C. C. Lucas, Banting Institute of Medical Research, University of Toronto, read composition in all chapters except the last, and his suggestions for construction of the text from the many different references were very helpful. For reading parts of the manuscript and for discussing technicalities grateful acknowledgment is made to: Mr. H. Whitehead, (Baker & Co., Inc.), Mr. A. Buchan (Bakelite Corporation of Canada Ltd.), Mr. Charles Owen Brown (Chemical Engineer, New York City), Mr. A. F. G. Cadenhead (Shawinigan Chemicals Limited), Mr. R. O. Campbell (British American Oil Co. Ltd.), Mr. O. B. J. Fraser (International Nickel Co., Inc.), Professor A. R. Gordon (University of Toronto), Dr. B. F. Haanel (Department of Mines and Resources, Ottawa), Dr. L. F. Marek (Arthur D. Little, Inc.), Professor R. R. McLaughlin (University of Toronto), Mr. J. E. Lee (Consumers' Gas Company, Toronto), Dr. F. Hugh Lawford (Standard Brands Ltd.), Mr. A. O. Hutton (Standard Chemical Co. Ltd.), Dr. J. D. von Mikusch (Woburn Degreasing Co. of New Jersey), and others.

Acknowledgment is due to Mr. W. R. Wallace, Chief Librarian, and his staff, in the library of the University of Toronto; and to the staff of the Hallam Room and the Patent Department of the Public Library, in the City of Toronto. Much assistance in typing and work on the manuscript was received from Miss Doris Birkett, Secretary and Librarian, Department of Chemical Engineering, University of Toronto, for which the author wishes to express very sincere thanks. The considerable reference work was made possible by the untiring assistance I have received from my wife who gave whatever time was required to assist in searches, abstracting, making of the bibliographies, etc. For all this assistance the author expresses his grateful thanks.

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TABLE OF CONTENTS

PAGE

FOREWORD iii

AUTHOR'S PREFACE v

LIST OF ILLUSTRATIONS xiii

INTRODUCTION 1

CHAPTER I. Brief History of Catalytic Chemistry 4

CHAPTER II. Catalytic Theory 9
- 1. Introduction 9
- 2. Chemical Composition (Purity) 10
- 3. Spectroscopic Methods in Catalytic Technique 19
- 4. Surface Reactions 25
- 5. Positive Catalysis 35
- 6. Negative Catalysis 35
- 7. Autocatalysis 38
- 8. Chain Reactions 41
- 9. Induced Reactions 46
- 10. Induction Periods 46
- 11. Promoters 48
- 12. Inhibitors 52
- 13. Catalyst Poisons 54
- 14. Homogeneous Catalytic Reactions 59
  - a. Homogeneous Catalytic Chain Reactions 63
  - b. Homogeneous Vapor and Gas Reactions 67
  - c. Homogeneous Reactions in Liquid Phase 70
  - d. Acid-Base Catalysis 70
  - e. Salt Effects 72
  - f. Solvent Effects 75
  - g. Hydrolytic Reactions 77
  - h. Catalysis in Intramolecular Changes 77
- 15. Heterogeneous (Contact) Catalytic Reactions 81
  - a. Phases 82
  - b. Adsorption 83

PAGE

CHAPTER II. Catalytic Theory (*Cont.*)
c. Desorption 89
d. Activity 91
e. Selectivity 95
f. Specificity of Surfaces 99
g. Energy of Activation 103
h. Heterogeneous Catalytic Chain Reactions 106
i. Wall Reactions 107
16. Catalysis in Solids 109
17. Catalysis in Mixtures 111
18. Periodic Reaction Changes 112

CHAPTER III. Nature and Properties of Catalysts 115
Introduction 115
The Chemical Elements and Compounds in Catalysis 123
Hydrogen 123
Group I: Li, Na, K, Rb, Cs, Cu, Ag, Au 129
Group II: Be, Mg, Ca, Sr, Ba, Ra, Zn, Cd, Hg 133
Group III: B, Al, Ga, In, Tl, Sc, Y, Rare Earths, Ac 135
Group IV: C, Si, Ge, Sn, Pb, Ti, Zr, Hf, Th 139
Group V: N, P, As, Sb, Bi, V, Cb, Ta, Pa 141
Group VI: O, S, Se, Te, Po, Cr, Mo, W, U 144
Group VII: F, Cl, Br, I, Mn, Ma, Re 148
Group VIII: Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt 149
Mixed Catalysts 170
Carriers 173

CHAPTER IV. Specific Types of Catalytic Reactions 184
1. Oxidation 184
2. Dehydrogenation 204
3. Cyclization 212
4. Hydrogenation 219
5. Hydration 235
6. Hydrolysis 237
7. Dehydration 242
8. Esterification 244
9. Halogenation 249
10. Alkylation 252
11. Isomerization 261
12. Condensation 266
13. Polymerization 275

PAGE

CHAPTER IV. Specific Types of Catalytic Reactions (*Cont.*)
14. Sulfonation 286
15. Desulfurization 288
16. Amination 291
17. Ammonolysis 294
18. Enzymes and Organic Catalysts 295

CHAPTER V. Industrial Catalytic Reactions 304
1. Catalytic Reactions in the Synthetic Nitrogen Industry .. 304
2. Acetylene Derivatives 324
3. Products from Carbon Oxides and Water Gas 329
4. Natural Gas 339
5. Production of Alcohols 340
6. Cracking of Coals, Tars and Oils by Hydrogenation at High Temperatures and Pressures 348
7. Production of Motor Fuels 360
8. Synthetic Rubber 383
9. Catalytic Hydrogenation of Vegetable and Animal Oils and Fats 396
10. Hydrogenation of Fatty Acids and Oils for Production of Higher Alcohols and Esters 410
11. Dehydration of Castor Oil 412
12. Catalytic Hydrolysis of Oils and Fats 417
13. Formation of Carboxylic Acids 423

Title [redacted]

Author [redacted]

Accession No. [redacted]

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Borrower's No.	Issue Date	Borrower's No.	Issue Date

LIST OF ILLUSTRATIONS

FIGURE NO.	CAPTION	PAGE
1.	Absorption Curves for Various Hydrocarbons	20
2.	Standards for Ultraviolet Conjugation Assays	21
3.	Ultraviolet Absorption of Isomerized Linseed Acids	22
4.	Installation for Organic Quantitative Spectrum Analyses by Means of the Consolidated Mass Spectrometer	23
5.	Mixed Substances as Catalysts	50
6.	Scheme of Desorption Mechanism	90
7.	Apparatus for Multiple Hydrogenation Tests	94
8.	High-Pressure Reaction Bomb for Laboratory Experiments	96
9.	High-Pressure Reaction Bomb for Hydrogenation Reactions	97
10.	Cross Section of a Continuous Catalyst Reduction Furnace	153
11.	Wurster and Sanger Catalyst Plant for Wet Reduction of Nickel Formate	156
12.	Temperature Record of the Reduction of Nickel Formate in Oil at a Maximum Temperature of 464° F.	157
13.	Nickel Compounds for Catalytic Use	159
14.	Conversion Efficiency of Platinum-Rhodium Alloys	163
15.	Loss of Catalyst (Pt and Pt-Rh)	164
16.	Conversion Efficiency of Pt and Pt-Rh Catalysts at Various Gauze Temperatures	165
17.	Mixed Molybdenum Catalysts	171
18.	Theoretical Magnesium-Substituted Montmorillonite	180
19.	TCC Synthetic Bead Catalyst	181
20.	Isocel Catalyst	182
21.	Flow Diagram of Aviation Naphtha Production by High-Pressure Hydrogenation	364
22.	Flow Sheet of Hydrogenation Section	365
23.	Fluid Catalyst Cracking Plant	368
24.	Single-Stage System	370
25.	Two-Stage Countercurrent System	371

FIGURE NO.	CAPTION	PAGE
26.	Flow Diagram of Sulfuric Acid Alkylation Plant ..	380
27.	Flow Diagram of Three-Stage Sulfuric Acid Alkylation Plant, Split-Olefin Feed	382
28.	Martinez Alkylation Plant of Shell Oil Company ...	383
29.	Hydrogenation Plant Using Nickel Formate Catalyst	399
30.	Hydrogenation Plant Showing Reducer, Mixing Tank, Filter Press, and Converter	400

INTRODUCTION

THE velocity of chemical reactions may be increased or decreased by the presence of small amounts of substances which do not enter into the resulting compound. Thus, a catalyst is defined as a substance which, by its presence in a medium where a chemical reaction takes place, either increases or decreases the reaction velocity without being changed itself or appearing in the compound resulting from the reaction. Consequently, a catalyst may enter into the reaction over and over again. This definition includes the effect of solvents or gaseous reaction media which may act as catalytic substances. If the catalytic effect is combined with selectivity, i.e., with specific choice in the combination of the reacting substances, the catalyst also directs the course of the reaction. In the majority of positive catalytic reactions, the catalyst causes chemical reactions to take place at an energy level lower than that at which they would occur, without the catalyst. Sometimes, catalysis is due to the transfer of energy of activation from energy-rich molecules. A chemical reaction, the velocity of which is influenced by a catalyst, is called a catalyzed or catalytic reaction, and the phenomena involved in all such reactions are called catalysis.

In the study of catalysis, besides the physical factors influencing chemical reactivity, the presence of substances, other than those accounted for in the empirical formulae for pure compounds, must be considered, as such substances may influence the mechanism of the reactions by either accelerating or retarding or concurrently retarding and accelerating, the reaction velocity. How this is accomplished is studied in catalytic chemistry. In this connection, it is well to bear in mind that formula-pure chemical compounds have never been prepared, the closest approaches being attained with critical standard substances.[1]*

Catalytic phenomena, in natural processes, are widespread, but only partly understood. The possible rôle of catalysis in reactions in the core and the crust of the earth is revealed in the magnificent pioneering works of Moissan [2] and Ipatieff,[3] the former studying reactions in the electric furnace and the latter reactions at high temperatures and pressures. It is doubtful that catalysis is very active at high temperatures, but in the cooling crust of the earth, there is a region where comparatively high pressures and temperatures exist, providing conditions comparable to those of high-temperature and high-pressure catalysis, and it is in this zone of the earth's crust that natural gas and petroleum products are likely to be formed, as discussed by Ipatieff.[3] In the weathered surface-crust of the earth, catalysis is, no doubt, of considerable importance, since many colloidal substances, formed by the weathering processes, are the same as those which are recognized as catalysts in chemical reactions studied up to now, e.g., colloidal aluminum silicates, hydrous alumina, hydrous iron oxides, silicic acid gels, humic acids and other organic colloids, enzymes from microorganisms and plant roots, etc. The cells of plant roots accumulate a very high concentration of minerals from dilute soil solutions and so do algae in pond water, this process undoubtedly being catalytic and, perhaps, due to acid-base catalysis.

One of the most important catalytic mechanisms is that associated with the green pigment in plants, i.e., chlorophyll, with the help of which plants can synthesize sugars and higher carbohydrates from atmospheric carbon dioxide and water. In all living organisms, i.e., microorganisms, plants, and animals, the vital metabolic processes are made possible by means of organic catalysts of purely chemical nature and of enzymes, the latter being named, according to their functions, esterases, proteases, dehydrogenases, oxidases, etc. It can truly be said that the living cell is the most efficient synthetic laboratory, known to man, and as time marches on, increasing inspiration for further development of chemical reaction technology is likely to arise from a study of nature's own processes. These problems will be treated in another book, now in preparation, concerning the chemical and catalytic action of compounds.

---

* Numbers above the line indicate literature references.

[1] Lohse, H. W.: *Sands, Clays and Minerals*, **2**, 133 (1936); *Canadian Mining Journal*, March, 1940.

[2] Moissan, H.: *The Electric Furnace*, London, Edward Arnold, 1904.

[3] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures*, New York, The Macmillan Company, 1937

CHAPTER I

BRIEF HISTORY OF CATALYTIC CHEMISTRY

THE alchemical concept, in the middle ages, was one of catalysis in a philosophical and metaphysical sense. The use of the philosopher's stone, for transformation of base metals into "gold" and for providing health and long life, was a catalytic concept, derived from medicine, where it was recognized that certain drugs assisted in the processes of the living organism. The preparation of ether, by the action of sulfuric acid on alcohol, was known to the alchemists, who made the necessary acid by combustion of a mixture of sulfur and niter. In the middle of the 18th century, Roebuck and others introduced the chamber process for the manufacture of sulfuric acid, by oxidation of sulfur dioxide, in the presence of small amounts of nitrogen oxides. The saccharification of starch, by acids, was discovered by Parmentier, in 1781. Both of these processes were not elucidated until later, the sulfuric acid process by Clement and Desormes, in 1806 and the saccharification process by Doebereiner, in 1806 and by Kirchoff, in 1812.

Until the discovery, by Lavoisier, of the chemical nature of combustion and of the composition of water, at the end of the 18th century, and the appearance of Dalton's atomic theory, in 1806, a basis for interpretation of catalytic phenomena did not exist. However, during the 19th century, catalytic phenomena attracted more and more attention. Scattered individual observations, during the first third of the century, were followed by Berzelius'[1] general recognition, in 1836, of the importance of catalysts and catalysis in chemical reactions. Berzelius observed that certain substances could induce chemical activity by their mere presence in a reaction medium and called this phenomenon "catalysis." It should be mentioned, however, that before Berzelius, scattered observations were recorded on catalytic phenomena, but it was Berzelius who verified the fact that catalytic phenomena were quite common in chemical reactions. Half a dozen years after Berzelius' recognition of catalysis, Mitscherlich[2] discussed "contact action," a phenomenon which had already been demonstrated by Faraday,[3] as early as 1834, who had observed previously that the essential condition, for the union of hydrogen and oxygen, in the presence of platinum, is that the metal has a clean, pure and metallic surface. Faraday had also demonstrated, in 1825, that ammonia could be catalytically synthesized from nitrogen and hydrogen. Kuhlmann showed, in 1839, that ammonia could be oxidized to nitric acid, with platinum as a catalyst.

---

[1] Berzelius: *Jahresber. Chem.*, **15**, 237 (1836).

The recognition of catalysis by Berzelius, the discovery by Pasteur, in the sixties, of the importance of microorganisms in fermentation, the development of physical chemistry, during the last half of the 19th century, and the utilization of catalysis in industry, led to the acknowledgment of the supreme importance of catalysis in chemical reactions, at the end of the 19th century. Ostwald[4] (1901) defined a catalyst as any substance which alters the velocity of a chemical reaction, without appearing in the end product and predicted that catalysis will have to be universally recognized in theoretical chemistry; he also foresaw that catalysis will have wide-spread industrial application. Then, Sabatier[5] and Ipatieff[6] began their pioneering researches in catalysis, thus opening up a field of chemistry and engineering which has enormous industrial consequences. Sabatier's pioneer work, in organic catalysis, often carried out under very simple conditions, has immense importance in organic synthesis. Ipatieff, working at high temperatures and pressures, recognized that the walls of the reaction vessel may greatly influence the chemical reaction. Haber's [7] researches appeared right after the turn of the century, and his exact experimental work and not less lucid and exact interpretation of reaction mechanisms gave a tremendous impetus to the early development of the synthetic industry, utilizing air and gases.

---

[2] Mitscherlich: *Liebigs Ann. Chem.*, **44**, 186 (1842).

[3] Faraday: *Phil. Trans.*, **114**, 55 (1834).

[4] Ostwald: *Z. Elektrochem.*, **7**, 995 (1901).

[5] Sabatier, P.: *La Catalyse en Chimie Organique*, Librairie Polytechnique, Paris, 1920. (Sabatier and Reid: *Catalysis in Organic Chemistry*, New York, D. Van Nostrand Co., 1923.)

[6] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures*, New York, The Macmillan Company, 1937.

Mittasch,[8] who pioneered in the preparation and application of catalysts, working with Haber and Bosch, has tabulated the data of the history of catalysis up to our time as follows:

I. Chronological data on catalytic research up to our time:

1781: Parmentier; hydrolysis of starches by means of acids (1808, Doebereiner; 1811, Kirchoff).

1806: Clement and Desormes; nitrogen oxides as accelerators of the oxidation of sulfur dioxide by air.

1817: H. Davy; the influence of heated platinum on combustible gases and vapors, and the detrimental factors influencing these reactions.

1818: Thenard; decomposition of hydrogen peroxide by platinum.

About 1820: Doebereiner; the catalytic action of platinum at ordinary temperature.

1823: Dulong and Thenard; the influence of metals on gas reactions (reduction of NO; Knallgas catalysis).

1834: Mitscherlich; decomposition of alcohol into ether and water under the influence of sulfuric acid.

1834: Catalysis of gas mixtures.

1836: Berzelius; name and definition of catalysis.

About 1860: Numerous catalytic reactions studied by Schoenbein.

1901: Ostwald; lecture on catalysis; new definition.

Since then, catalytic chemistry has been studied and further developed by a large number of scientific investigators whose work and accomplishments will be discussed in this book.

It is a peculiar fact that in the catalytic realm, applied chemistry has always been ahead of theoretical chemistry, a condition which still exists. This is chiefly due to the fact that catalytic phenomena, as yet, are not fully understood, the major reason being that catalysis is caused by the presence of comparatively small quantities of a substance or substances in the reaction system, and the matter of the chemical purity of the reactants, in chemical reaction systems, has not been properly considered. Consequently, until spectroscopic and other sensitive physical and chemical analytical methods will be as commonly used as the usual analytical methods, there is not much hope that catalytic reactions can be truly interpreted and understood.

---

[7] Haber, F.: *Thermodynamics of Technical Gas Reactions,* London, Longmans, Green & Co., 1908.

[8] Mittasch: *Ber.,* 59, 27 (1926).

Mittasch[8] tabulates the history of industrial catalysis as follows:

II. Chronological data on industrial catalysis up to our time:

1868: Deacon and Hurter; catalytic production of chlorine from hydrochloric acid and air.

1875: Clemens Winkler; oxidation of SO_2 to SO_3 with air, in the presence of a platinum contact.

1882: Tollens and Loew (Merklin factory); catalytic oxidation of methyl alcohol to formaldehyde.

1885: Chance and Claus; catalytic oxidation of hydrogen sulfide to sulfur.

1890: Badische Anilin-und Sodafabrik, R. Knietsch; SO_3-contact with roast gases and platinum contact.

1895: Badische Anilin-und Sodafabrik, Sapper; catalytic production of phthalic acid by oxidation of naphthalene in the presence of mercury.

1898: Verein Chemischer Fabriken, Hasenbach and Clemm; substitution of iron oxide for platinum in the SO_3-process.

1901: Polzenius; addition of chloride in the combination of nitrogen with calcium carbide to form cyanamide.

1902: Normann; foundation of the catalytic hydrogenation of oils and fats in liquid medium.

1903: W. Ostwald; production of nitric acid by catalytic oxidation of ammonia on a platinum contact.

1907: Raschig; catalytic production of hydrazine.

1908: Catalytic high-pressure synthesis of ammonia.

About 1910: Gruenstein (according to Wunderlich); acetaldehyde from acetylene.

1910–14: Badische Anilin-und Sodafabrik; activated contact masses for the ammonia synthesis; technical accomplishment of the high-pressure synthesis by C. Bosch.

1913: Badische Anilin-und Sodafabrik; catalytic production of hydrogen from carbon monoxide and water; catalytic carbon monoxide reduction under pressure to different organic compounds; catalytic reduction of nitrobenzene to aniline.

1914: Badische Anilin-und Sodafabrik; catalytic ammonia oxidation with iron oxide—bismuth oxide.

1916: Wohl, Gibbs; phthalic acid and anthraquinone by partial catalytic oxidation.

1917: Farbenfabriken vorm. F. Bayer; catalytic oxidation of hydrogen sulfide by means of activated carbon, in the presence of ammonia.

1918: Frazer; carbon monoxide oxidation at ordinary temperature by means of Hopcalite (Cu-Mn-oxide; Cu-Mn-Ag-oxide).

1923: Badische Anilin-und Sodafabrik; catalytic methanol production.

1924–25: Badische Anilin-und Sodafabrik; production of hydrocyanic acid from carbon monoxide and ammonia or formamide.

Since the first world war, catalytic chemistry, in theory as well as in practice, has advanced tremendously in the United States, and these developments are creating chemical history almost daily.

GENERAL REFERENCES

(1) G. M. Schwab (with H. S. Taylor and R. Spence): *Catalysis from the Standpoint of Chemical Kinetics*, New York, Van Nostrand & Company, 1937. (2) T. P. Hilditch and C. C. Hall: *Catalytic Processes in Applied Chemistry*, London, Chapman & Hall, 1937. (3) Rideal, E. K. and H. S. Taylor: *Catalysis in Theory and Practice*, London, Macmillan & Co., Ltd., 1919.

CHAPTER II

CATALYTIC THEORY

1. Introduction

Although the nature of the phenomena, associated with catalytic reactions, is only partly understood, it is useful to view the factual results in the light of chemistry, physics and mathematics, as it is done in chemistry, in general.

There is still a considerable way to go, before reaction kinetics can be interpreted from a catalytic point of view, the major reason being that knowledge of the influence of impurities and the reaction products on the reaction mechanisms is still deficient.[1]

Except for the requirement of the presence of an extraneous substance, a catalytic reaction follows the fundamental chemical and physical laws. Brönsted[2] assumed, in 1922, that catalytic reactions, and possibly all reactions, proceed by the formation of a *critical complex,* which decomposes into the substances resulting from the reaction, viz.:

$$A + B \rightarrow X \rightarrow C + D$$

where A and B are the reactants, X the critical complex, and C and D the resulting substances. The formation of the critical complex is slow and determines the velocity of the reaction. The formation of X depends on the activities of A and B, and the reaction velocity is expressed by

$$v = k a_A a_B \cdot \frac{1}{f_x}$$

where a_A and a_B are the activities of A and B, f_x is the activity coefficient of X and k is a constant. Bjerrum[3] deduced a similar equation, assuming that concentrations and not activities determine the velocity of reaction. (See also Acid and Base Catalysis, p. 70.) The formation of intermediate reaction products, in catalytic reactions, was originally suggested, in the eighties, by Armstrong[5] and Arrhenius.[6]

---

[1] Lohse: *Can. Mining J.*, December, 1938.

[2] Brönsted: *Z. physik. Chem.*, 102, 169 (1922).

[3] Bjerrum: *Ibid.*, 108, 82 (1924); *ibid.*, 118, 251 (1925).

These conceptions are in harmony with those of Mittasch[4] who calls attention to the fact that many non-catalytic chemical reactions proceed through successive stages and through formation of intermediate compounds in the same way as many, if not all, catalytic reactions do.

Ostwald[7] stated that there is probably no kind of chemical reaction which cannot be influenced catalytically, and there is no substance, element or compound which cannot act as a catalyst. Considering the fact that most of our chemical knowledge, today, is derived from observing substances which are not atomically pure, there is probably much truth in Ostwald's conclusion.

2. Chemical composition (purity)*

Due to the fact that the presence of minute quantities of some substance or other may influence the velocity of a chemical reaction, and, at times, also the direction of a chemical reaction, it is of vital significance that the presence of these minor constituents in the reacting substances and their role in the reactions should be interpreted and accounted for.

Ostwald[1] wrote early in this century that the observed predominance of positive catalysts is to be ascribed to the fact that very pure substances often react extremely slowly with each other, and that the active amounts of catalytic substances are often very much smaller than could be detected by the analytical methods available at the time. Since then, analytical technique for estimating minute quantities of chemical elements and compounds has advanced tremendously, and the horizon of analytical estimation has been widened to include almost imponderable quantities.

---

[4] Mittasch: *Ber.*, **59**, 13 (1926).

[5] Armstrong: *Proc. Roy. Soc. (London)*, **40**, 287 (1886).

[6] Arrhenius: *Z. physik. Chem.*, **4**, 226 (1889).

[7] Ostwald: *Z. Elektrochem.*, **7**, 998 (1901).

* Part of this section was read as a paper before the Spring Meeting of the Section of Industrial and Engineering Chemistry of the American Chemical Society, Cleveland, Ohio, April, 1944.

[1] Ostwald, W.: *The Fundamental Principles of Chemistry*, London, Longmans, Green & Co., 1909.

The word "chemical purity" is connected with the thought of *absence* of constituents other than the substance in question. Whereas this term is logical when using it in refining of substances, this is not the case when thinking of the chemical properties and particularly of the reactivity of substances, because of the fact that small quantities of foreign matter may influence the reactivity of a substance very considerably. Furthermore, the last traces of foreign matter, present in the original mother substance of any refined material, are not readily removed and likely never absolutely so, consequently, atomically pure substances have never been made. As all chemists know, a gram-molecule (mol) of any substance contains 6.05×10^{23} molecules, and the attempt to sort out each and every single foreign molecule which is found in one gram-molecular weight of any substance is a task in which the odds are against success. If we consider that the analytical range of substances, such as we work with them in the laboratory and plant, as being from one to 0.0001 per cent, the number of molecules present in one mol is approximately as follows, the mol for simplicity's sake considered to contain 10^{24} molecules and the minor constituents as being of the same average weight as the mother substance:

Percentage of minor constituent		Number of single molecules
One mol	$= 10^{24}$	1,000,000,000,000,000,000,000,000
1	$= 10^{22}$	10,000,000,000,000,000,000,000
0.1	$= 10^{21}$	1,000,000,000,000,000,000,000
0.01	$= 10^{20}$	100,000,000,000,000,000,000
0.001	$= 10^{19}$	10,000,000,000,000,000,000
0.0001	$= 10^{18}$	1,000,000,000,000,000,000

A very good idea of the tenacity, with which the original chemical composition manifests itself, is seen from the following tables presenting spectroscopic investigations of iron minerals (46 analyses of iron sulfides and oxides)[2] and highly refined iron (spectroscopic and chemical analyses).[3]

Chemical elements ascertained in 46 spectograms of iron minerals, sulfides and oxides (Fitch):[2] *

I	II											III	IV	V	VI	VII
Li	—											—	—	—	(O)	—
Na	—											—	—	—	S	—
K	Ca	—	—	—	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—	—	—	—
Rb	—	—	—	—	—	—	Ru	Rh	Pd	Ag	—	In	—	—	—	—
--	—	—	—	--	—	—	Os	Ir	Pt	Au	--	—	Pb	—	—	—
—	—	—	Th	—	—		Rare earth elements									

Chemical elements ascertained spectroscopically and chemically in very pure iron (Judd Lewis) (Total minor constituents = 0.2655 and traces.):

—	—											B	C	—	—	—
												.0002	.015			
—	Mg											—	Si	P	S	—
	mtr												mtr	.016	.045	
—	Ca	—	—	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	—	As	—	—
	tr			mtr	.014	.022	99.73	.008	.022	.097	mtr	tr		.004		
—	—	—	—	—	Mo	—	—	—	—	—	—	—	Sn	Sb	—	—
					.011								.010	.0006		
—	—	—	—	—	W	—	—	—	—	—	—	—	Pb	Bi	—	—
					mtr								.0007	mtr		
—	—	—	—	—	—											

Note, tr = trace; mtr = minute trace. Numbers indicate percentage.

It should be noted that in the minerals, the spectroscopic analyses were not supplemented by chemical analyses as in the case of the pure iron, and for this reason, the metalloids are practically all absent. In the pure iron, the absence of the alkalies may be attributed to their volatilization during the refining process. Otherwise, the metallic elements are about the same in natural and refined iron.* By using even more refined chemical and spectroscopic technique, this picture would be even more striking.[3a]

Some other examples of composition of metals such as used in catalytic work are the following (spectroscopic analyses):

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[2] Fitch, A. A.: *Spectrum Analysis in Mineralogy*, London, Adam Hilger, Ltd.

[3] Lewis, S. Judd: *Spectroscopy in Science and Industry*, London, Blackie & Son, Ltd., 1933.

* The presence of precious metals in some spectrograms is due to inclusion of spectograms of Norwegian pyrrothites.

[3a] Lohse: *Can. J. Research*, **12**, 519 (1935); *Can. Mining J.*, December, 1938. *Sands, Clays, Minerals*, **2**, 133 (1936).

Technical copper (Barker):[4]

—	—											—	—	—	—
—	—											Al	—	—	—
—	—	—	—	—	—	Mn	Fe	—	Ni	Cu	Zn	—	—	As	—
—	—	—	—	—	—	—	—	—	—	Ag	Cd	—	Sn	Sb	—
		•													
—	—	—	—	—	—	—	—	—	—	—	—	—	Pb	Bi	—
—	—	—	—	—	—										

Very pure nickel (Twyman):[5]

—	—											B	C	—	—	—
Na	**Mg**											Al	Si	—	—	—
—	**Ca**	—	—	V	—	Mn	Fe	Co	Ni	Cu	Zn	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—	—	Sn	—	—	—
		•														
—	—	—	—	—	—	—	—	—	—	—	—	—	Pb	—	—	—
—	—	—	—	—	—											

Laboratory reagents are highly refined substances, nevertheless they contain impurities however pure they are. Some examples are given for a few chemicals of the highest purity from two leading manufacturers:

Chemical		Maximum impurities in per cent I	II
Acetic anhydride $(CH_3CO)_2O$	Non-volatile matter	0.0025	0.003
	Cl	0.001	0.0005
	SO_4	0.002	0.0005
	Heavy metals as Pb	0.002	0.0005
	Fe	0.001	0.001
	P	0.0005	PO_4 0.001
Aluminum chloride, anhydrous $AlCl_3$	SO_4	.....	0.003
	Heavy metals as Pb	.....	0.001
	Fe	.....	0.002
	Cl	.....	0.005
Nickel sulfate $NiSO_4.6H_2O$	Heavy metals as Pb	0.004	.....
	Fe	0.001	0.01
	Co	0.0005	0.05
	Alkalies and alkaline earths	0.1	0.20
	Ammonia	no reaction	.....
	NO_3	.....	0.005
	Cu	.....	0.01
	Zn	.....	0.05
	Insoluble	.....	0.01

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[4] Barker, F. G.: *Alloy Steels*, Chapter 4, "Spectographic Analysis in Great Britain," by A. C. Candler. London, Adam Hilger Ltd., 1939, p. 15.

* Rarer earths.

[5] Twyman, F.: *The Spectrochemical Analysis of Metals and Alloys*, London, Charles Griffin & Company, Ltd., 1941.

It is noteworthy that the contents of minor constituents, in even the purest laboratory substances, are of an order of magnitude equal to what is considered significant in catalytic reactions where the presence of a substance in concentrations of 0.01 to 0.001 per cent, or much less, may have definite action. The presence of iron, in all of the samples, is significant in this connection because small amounts of iron have definite catalytic action in many cases. Iron, in fact, is a minor constituent in most substances.

The catalytic action of organic substances has not been studied to the same extent as that of inorganic substances, but at times, exceedingly small amounts of an organic substance can influence the reaction velocity very considerably. Thus, it has been found that piperidine and ammonia, in a concentration of N/10,000,000, greatly influence the rate of change of keto-enol isomerism of aceto-acetic ester at room temperature. With a concentration of the catalyst of 4 × 10^{-5} mol, the ratio of rate of change, in this reaction, was for various catalysts (K_1 = velocity constant of non-catalyzed reaction; K_2 = velocity constant of catalyzed reaction):[6]

Catalyst	K_2/K_1
Piperidine	11,400
Ammonia	4,000
Pyridine	264
Quinoline	17
Bromine	1,300

Reactions equally or more sensitive to the presence or absence of minute quantities of chemical substances are shown by biological systems. Thus, it was found that as little as 10 γ of molybdenum per liter of culture media stimulated the growth of Aspergillus niger.[6a] Minute traces of thiamin are required for the growth of several microorganisms, the optimum concentration for the growth of Ustilago violacea being 0.06 γ in 100 cc of the growth medium, i.e., 0.00,000,005 per cent. This very small quantity of thiamin causes, under the conditions described, the formation of 2,500,000 parts of Ustilago violacea to be formed per one part of thiamin.[6a] Other growth substances, vitamins and hormones, show similar action in so small quantities that they would not be taken into account if it were not for the biological phenomena caused by their absence.

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[6] Rice and Sullivan: *Trans. Faraday Soc.*, **24**, 554 (1928).

[6a] Schopfer, W. H.: *Plants and Vitamins*, Waltham, Mass., The Chronica Botanica Co., 1943.

In view of these facts, it is not correct to speak of chemical purity in the sense of *absence* of some substance, without referring to the method used for determining the absence of the substance in question, as it is most likely that traces, at least, of the impurity in the mother substance remain in the refined product. Consequently, it is more logical to use the term *minor constituent* than impurity as this term implies the *presence* of minor contents of substances which, as we have seen, may have a very definite action on the reactivity of the mother substance and, also a very definite biological action. For the same reason, it is more logical to speak of composition than of purity, the gradation being approximately as follows:

Composition of matter	Substance
Natural composition	Minerals and rocks Natural waters Weathered earth Soils Living organisms
Technical composition	Industrial raw materials
Standard composition	Standard substances of chemicals and metals Standard laboratory substances Standard medicinal and pharmaceutical substances
Trace composition	Minor constituents ascertainable by trace analysis or bio-assay only
Ultra-trace composition	Constituents not ascertainable by present methods of measurement

With a view to these considerations, it may be stated 1) that a very large proportion of all the chemical elements known are probably present in most natural substances; 2) evidence, from observed cases of trace catalysis, points to the assumption that the chemical reactivity of substances decreases when minor constituents are removed below a certain threshold value; 3) in order to truly interpret the catalytic action of a small content of a substance or substances in a reaction system, its total composition, at least down to trace composition, should be known.

Water, which has been distilled once or twice under ordinary laboratory conditions, contains from 20,000 to 30,000 dust particles per cc,[7, 8, 9, 10, 11] and probably also minute traces of metals from the still, e.g., Zn.[6a] In view of this, and also considering the catalytic action of the walls of the apparatus used, it is doubtful that true homogeneous reactions are as widespread as it would appear from a study of literature on catalysis at this time (1942). Similar conclusions were published by Rice in 1926.[11]

One fact is certain, and that is that all the substances, we deal with in our chemical studies, are *mixtures*, and with increasing recognition of this fact it will be gradually revealed to what extent we will have to modify our conceptions with respect to the chemical reactivity of elements and compounds.

Armstrong[12, 13] assumed that chemical interchange is depending on the presence of a small content of an electrolytic impurity in the reaction system, this indispensable impurity being termed a determinant, ($\varepsilon\delta$), the equation of chemical change being as follows:

$$A_2 + \varepsilon\delta + B_2 \rightarrow AB + AB + \varepsilon\delta$$

If a catalyst (K) takes part in the reaction, the equation is written:

$$A_2 + \varepsilon\delta K + B_2 \rightarrow AB + AB + \varepsilon\delta K$$

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[7] Martin: *J. Phys. Chem.*, **24**, 478 (1920).

[8] Martin and Lehrman: *Ibid.*, **26**, 76 (1922).

[9] Kenrick: *Ibid.*, **26**, 72 (1922).

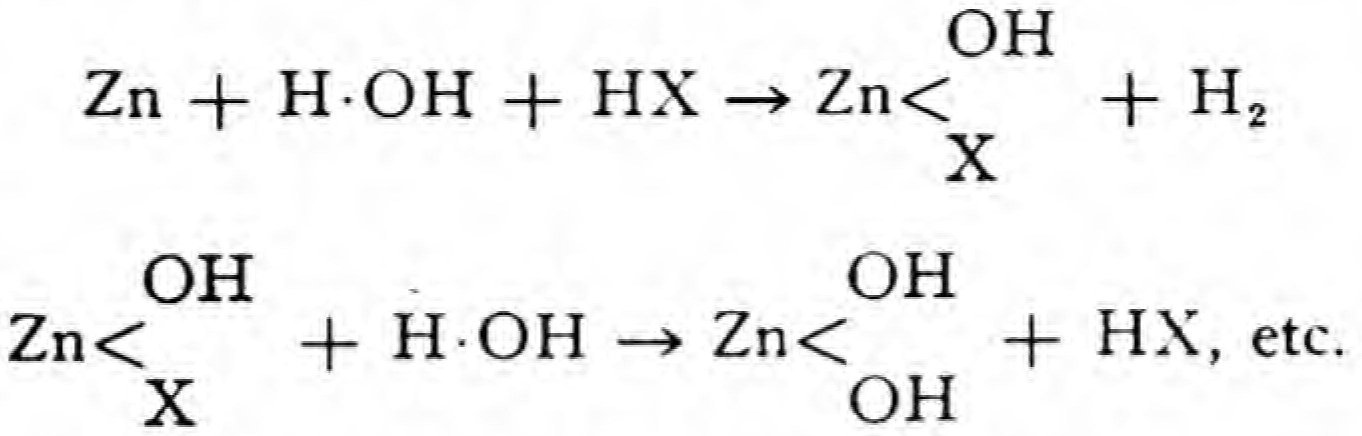
[10] Wolski: *Kolloidchem. Beihefte*, **13**, 137 (1920). (Ref.). Kenrick, *J. Phys. Chem.*, **26**, 72 (1922).

[11] Rice: *J. Am. Chem. Soc.*, **48**, 2099 (1926).

[12] Armstrong, H. E.: *Essays on the Art and Principles of Chemistry Including the First Messel Lecture*, London, Ernest Benn, Ltd., 1927.

[13] Armstrong: *J. Soc. Chem. Ind., Jubilee No.*, 1931, p. 179.

Of course, these equations elucidate the part played by the determinant and the catalyst only if the intermediate stages can be shown; and for this reason, Armstrong uses as an example the dissolution of zinc in distilled water in the presence of a small amount of acid, HX, the reaction scheme being as follows:



$$Zn + H\cdot OH + HX \rightarrow Zn{<}^{OH}_{X} + H_2$$

$$Zn{<}^{OH}_{X} + H\cdot OH \rightarrow Zn{<}^{OH}_{OH} + HX, \text{ etc.}$$

This reaction is really a chain reaction, and we would now be inclined to consider the acid as a catalyst, and the minor constituents, in the zinc, as being determinants. Based on recorded data for the minor constituents in zinc, the following elements have been found: Ag, As, Bi, C, Ca, Cd, Cu, Fe, In, Mg, O, Pb, S, Sb, Si. This indicates that the dissolution of zinc in dilute acid is a rather complicated process. The action is probably best explained as being galvanic, the galvanic cells being formed between the zinc and its minor constituents, e.g., $Zn/H_2SO_4/Cu$. In the case of Zn and Cu, the former acts as cathode (negative electrode) and the latter as anode (positive electrode). The acid medium constitutes the inner circuit, and the zinc metal the outer circuit. Such a mechanism will, of course, release zinc ions ($Zn + Cu^{++} \rightarrow Zn^{++} + Cu$). Hydrogen is then evolved on the zinc surface, and if the zinc is absolutely pure, it will be held there. However, this hydrogen film is broken by spots of impurities which act as depolarizers, either by not adsorbing the hydrogen (e.g., chromium), or by catalyzing the formation of hydroxonium ions, H_3O^+, with the water, the hydroxonium ion increasing the acid concentration, or by catalyzing or causing combination of atomic hydrogen to molecular hydrogen which is much more readily desorbed, or by oxidizing the hydrogen to water, if oxygen is present in the solution, etc.

It is also reasonable to assume that there is a galvanic action taking place on the surface of catalytic contact masses. The fact that at least a trace of water is indispensable in many heterogeneous catalytic reactions indicates this.[12, 13, 17, 17a] The function of such galvanic currents on the contact surface is then to induce polarization in a molecule coming into proximity of the surface, to orientate an already polarized molecule on the contact surface, to deposit and release metal ions according to their place in the electrochemical series, etc. Some minor constituents, e.g., oxides, metalloids, probably act as depolarizers combining unsaturated substances so that they are more readily desorbed, forming intermediary complexes or compounds which decompose readily and in this way facilitate desorption, and so on.

The specific chemical action of minor constituents, on a contact surface, was elucidated in several cases and the actual phenomena accounted for (nitride formation, page 101; carbide formation, page 102). Ipatieff[14] and Roginskii[15] both have found that small amounts of catalyst poisons may act as promoters. That is perfectly explainable, if the poison does not cover all of the active surface of the contact, but is present in just sufficient quantity to act as polarizer and/or depolarizer. In such a case, there will have to be a maximum activity of the surface when the spatial conditions of the different surface atom species are such that they fit the reaction scheme in question best. This concurs with Roginskii's finding that such maxima exist. Roginskii also found that degassed metals do not act as catalysts in the hydrogenation of ethylene.

The chemical-physical action, on a catalytic contact surface, is much enhanced by the very considerable amount of heat evolved during the chemical change on the surface. Thus, it has been found that, by complete hydrogenation of one mol oleic acid, the amount of heat evolved is of an order of magnitude of 89,000,000 calories per gram of active nickel (see page 411). In other words, the chemical reaction sphere, on contact surfaces, is probably a zone of higher temperatures than the surrounding medium. However, it takes a mechanism of chemical heterogeneity as described above to make reactions start and to keep them going. That again is facilitated by the heat evolved locally on the surface.

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[14] Ipatieff: *J. Phys. Chem.*, **45**, 431 (1941).

[15] Roginskii: *J. Phys. Chem., (U.S.S.R.)*, **15**, 1 (1941).

[17] Hinshelwood: *Trans. Faraday Soc.*, **24**, 554 (1928).

[17a] Bodenstein: *Z. phys. Chem.*, **B20**, 451 (1933); **21**, 469 (1933).

3. Spectroscopic methods in catalytic technique

The use of the spectroscope, as an investigational tool, is increasing rapidly,[1, 2] and although it is outside the scope of this book to discuss spectroscopic technique, some examples of practical investigations useful in catalytic work will be mentioned because these methods are so important for elucidation of reaction data.

Of the numerous applications of spectrographic analysis of metals and chemical compounds, spectrographic control has played a leading role in developing the gauze catalyst (Pt, Pt-Rh), used in the oxidation of ammonia to nitric acid,[3] which secures smooth running of the oxidation plant. The finished gauze is tested for purity before being sent to the plant, as it must be absolutely free of impurities that could be picked up in annealing, working or weaving. The returned gauzes are spectrographically examined for contaminations accumulated during the operations in the plant.

Infrared absorption spectra [4, 4a] in the region from 11,200 to 18,500 Å, where C-H vibrations are active, are recorded for hydrocarbons,[4] and quantitative data have been obtained with respect to the structural groups $—CH_3$, $>CH_2$, $\geqslant CH$, and $\geqslant CH$ (aromatic) of the infrared molal indices for 55 hydrocarbons. From data on known hydrocarbons, the absorption coefficients, for the various individual structural groups at appropriate wave-lengths, have been calculated. Infrared absorption spectra are also used for estimating the composition of high-octane gasoline (E.E.R.).

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[1] Twyman, F.: *The Spectrochemical Analysis of Metals and Alloys*, Charles Griffin & Co., Ltd., London, 1941.

[2] Brode, W. R.: *Chemical Spectroscopy*, John Wiley & Sons, Inc., New York, 1939.

[3] Strauss: *Amer. Soc. Testing Materials*, **35**, 11, 1935.

[4] Rossini: Proc. 18th Annual Meeting, *American Petroleum Institute*, Sect. III. Chicago, Ill., Nov. 11, 1937.

[4a] Barnes, Liddel, and Williams: *Ind. Eng. Chem., Anal. Ed.*, **15**, 659, 1943.

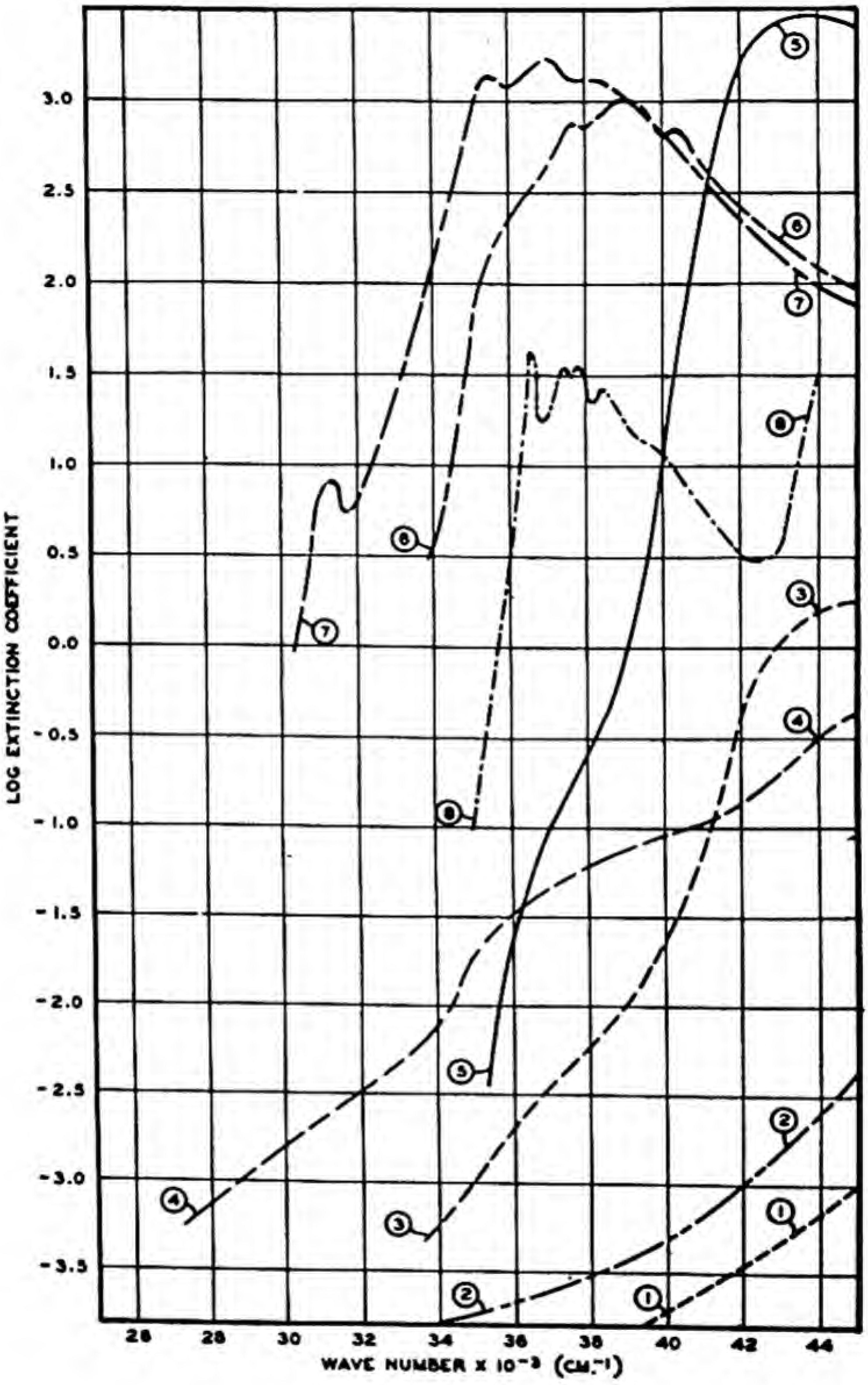

FIGURE 1

ABSORPTION CURVES FOR VARIOUS HYDROCARBONS

1. Hexane; 2. Cyclohexane; 3. 3-Hexene, contains some conjugated diene; 4. Cyclohexene, not free of dienes; 5. Dimethyl butadiene; 6. 1,3-Cyclohexadiene; 7. α-Eleostearic acid; 8. p-Cymene. (Bradley and Richardson.) (Reprinted by permission from *Ind. Eng. Chem.*)

Bradley and Richardson[5] used absorption spectra in the ultraviolet region for study of drying oils and resins, some of their data being presented in Figures 1–3.

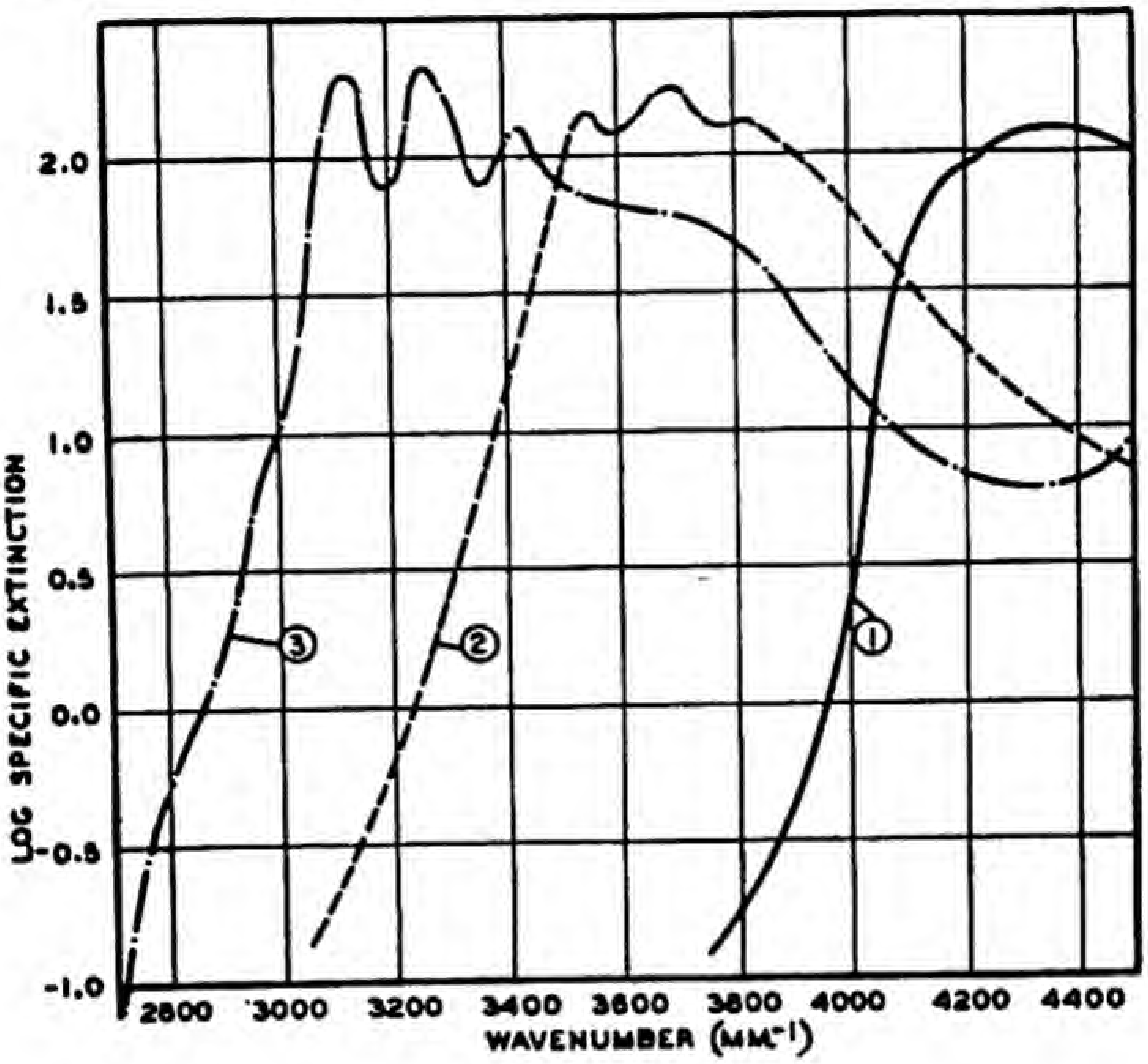

FIGURE 2

STANDARDS FOR ULTRAVIOLET CONJUGATION ASSAYS

(1) 9,11-Linoleic acid,
$CH_3—(CH_2)_6—(CH{=}CH)_2—(CH_2)_7—COOH$
(2) α-Eleostearic acid,
$CH_3—(CH_2)_3—(CH{=}CH)_3—(CH_2)_7—COOH$
(3) Parinaric acid,
$CH_3—CH_2—(CH{=}CH)_4—(CH_2)_7—COOH$

(Bradley and Richardson.) (Reprinted by permission from *Ind. Eng. Chem.*)

A spectrochemical analytical technique for quantitative organic analyses by means of mass spectrograms has been developed by The Consolidated Engineering Corporation who have designed a mass spectrometer for this purpose.[6a]

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[5] Bradley and Richardson: *Ind. Eng. Chem.*, **32**, 963, 1940; Ibid., **34**, 237, 1942.

[6a] Washburn, Wiley and Rock: *Ind. Eng. Chem., Anal. Ed.*, **15**, 541, 1943.

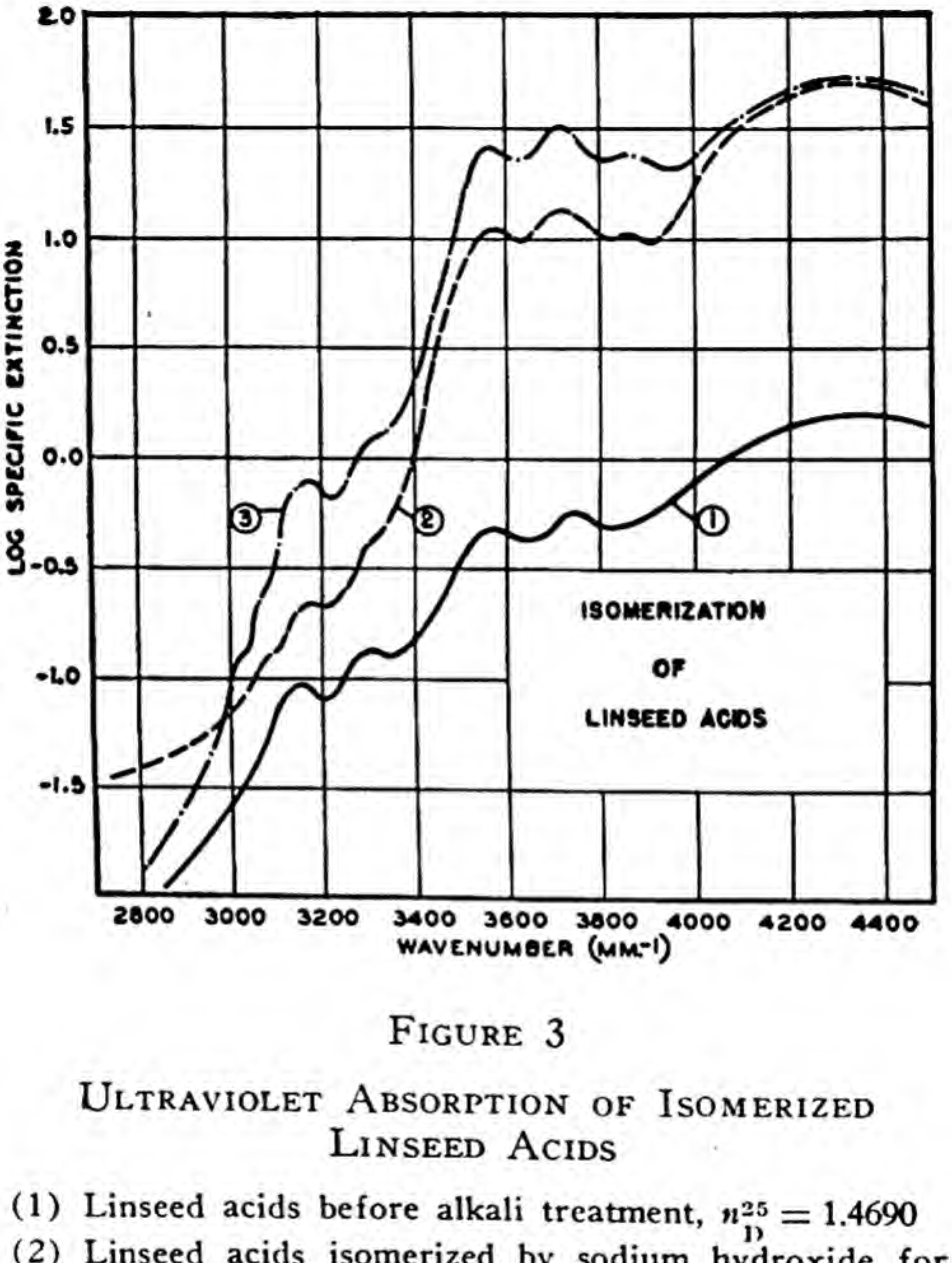

FIGURE 3

ULTRAVIOLET ABSORPTION OF ISOMERIZED LINSEED ACIDS

(1) Linseed acids before alkali treatment, $n^{25}_{D} = 1.4690$
(2) Linseed acids isomerized by sodium hydroxide for 3 hours at 225° C, $n^{25}_{D} = 1.4746$
(3) Distillation fraction from isomerized linseed acids, 180–90° C, at 1 mm, $n^{25}_{D} = 1.4850$

(Bradley and Richardson.) (Reprinted by permission from *Ind. Eng. Chem.*)

The mass spectra are recorded photographically on sensitized paper in a recording oscillograph. The error in recording is 0.3% or less of the value recorded for wide variations in magnitude of the peaks. A very small sample only, as little as 0.1 cc, is required for analysis. In the following table analytical data by ordinary chemical analyses are compared with a mass spectro-

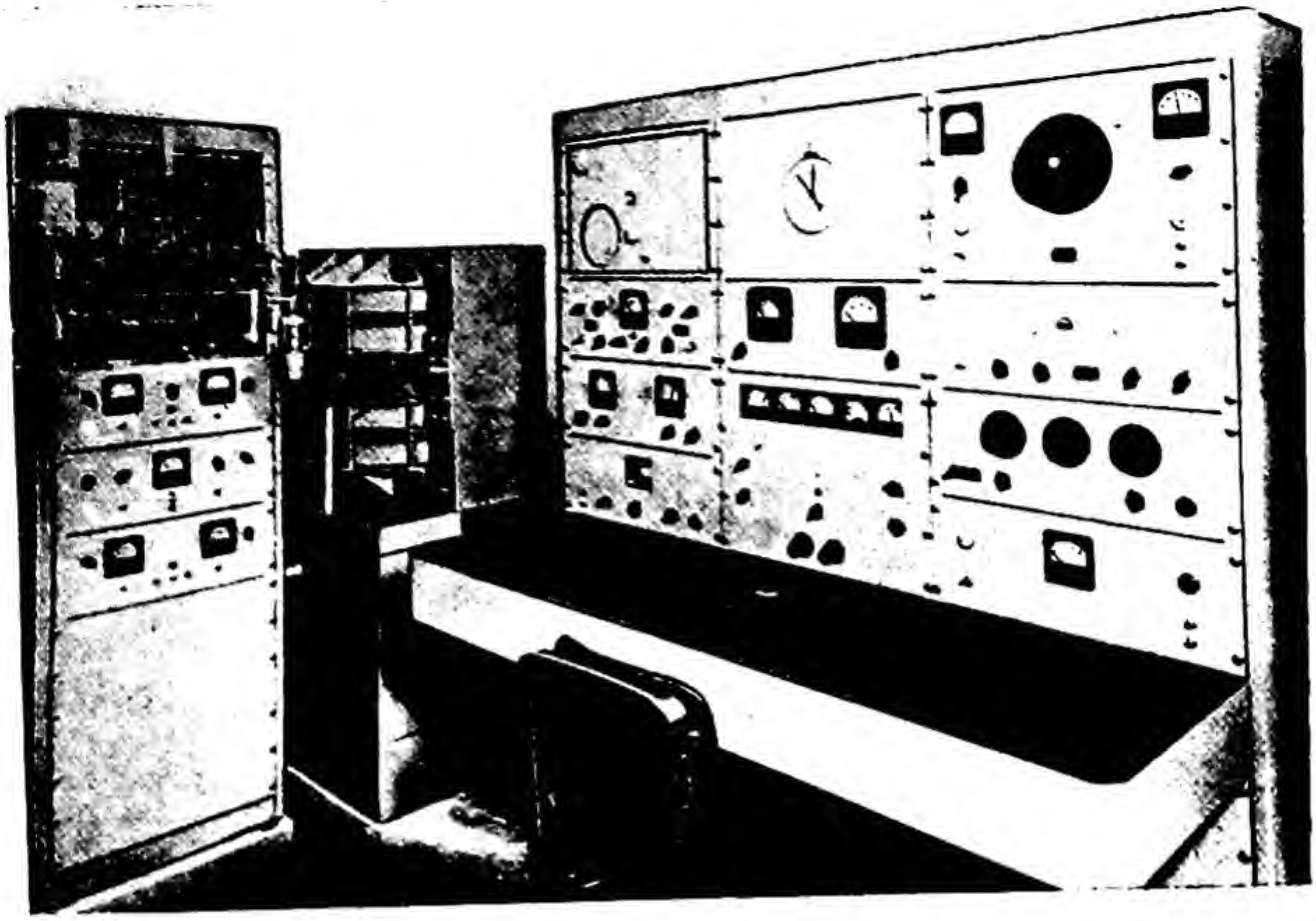

FIGURE 4

INSTALLATION FOR EXECUTING ORGANIC QUANTITATIVE SPECTRUM ANALYSES BY MEANS OF THE CONSOLIDATED MASS SPECTROMETER

In the center rear of this mass spectrometer is an electromagnet which produces a uniform magnetic field in which the spectrometer proper is placed. To the left of the magnet is the inlet apparatus for introducing the gaseous and liquid materials into the mass spectrometer. In the right foreground are the operator's table, the control panels, and the equipment cabinets. The cabinets house the automatic recording apparatus, the automatic mass marker, and the power supplies, with control circuits which furnish voltages to the mass spectrometer and electromagnet. (Courtesy of Consolidated Engineering Corporation, Pasadena, California; reprinted by permission from *Ind. Eng. Chem., Anal. Ed.*, September, 1943.)

chemical analysis of the same sample. The detection and estimation of components not discernible by ordinary chemical methods should be noted. For further details as to this method reference is made to the original paper.

Wet gas was analyzed and the mass spectrometer analysis compared with the results obtained on two fractionating columns.

The presence in the mixture of an unexpected component, viz., acetone, was definitely established by the mass spectrometer analysis. The figures in the table indicate mol per cent:

Component	Fractionating column A Mol per cent		Fractionating column B Mol per cent		Mass spectrometer Mol per cent
H_2					0.2
N_2					0.4
O_2					0.2
CH_4	91.500	91.600	91.517	91.557	89.9
C_2H_6	4.395	4.210	4.372	4.326	4.1
C_3H_8	1.492	1.942	1.968	1.969	2.0
iso-C_4H_{10}	0.612	0.583			1.0
			1.255	1.262	
n-C_4H_{10}	0.619 1.231	0.699 1.282			0.5
iso-C_5H_{12}	0.290	0.272			0.1
			0.491	0.488	
n-C_5H_{12}	0.227 0.517	0.222 0.494			0.2
C_6	0.232	0.250	0.236	0.230	..
C_{7+}	0.149	0.162	0.161	0.168	..
C_3H_6O (Acetone)	....	....	....	....	1.4

Total Time for Analysis = 2¼ hours including 30 minutes of mass spectrometer time.

Abel, Schmid and Stein [7] determined spectroscopically the equilibrium between HNO_3, NO and NO_2:

$$2HNO_3 + NO \rightleftarrows 3NO_2 + H_2O$$

The equilibrium pressure of NO_2 was determined spectroscopically by means of the NO_2 absorption spectrum of the gases in the equilibrium system. These absorption spectra were compared qualitatively and quantitatively (by means of intensities) with standard spectra, and the equilibria computed by means of the thermodynamic equilibrium constant:

$$K = \frac{a^3_{NO_2} \cdot a_{H_2O}}{a^2_{HNO_3} \cdot a_{NO}}$$

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[7] Abel, Schmid, and Stein: *Bunsen Society Meeting, Heidelberg, 1930.* Spectroscopy and Molecular Structure, p. 128.

Eisenhut and Konrad[6] studied the decomposition and formation of hydrocarbons in discharge tubes by means of canal rays. Atoms, molecules, and molecule fragments can leave the discharge vessel and be separated in an adjacent, high-vacuum container by means of electric and magnetic fields, and be observed, by known methods, according to mass and charge. The photographic plate, used in these experiments, was the Agfa-Autolith. The table gives an example of the data obtained by this method:

Decomposition products
[The numbers express mass (weight)]

Starting material	H	C	CH	CH_2	CH_3	C_2	C_2H	C_2H_2	C_2H_3	C_2H_4	C_2H_5
CH_4	1	12	13	14	15	..	..	..	..	..	..
C_2H_6	1	12	13	14	15	24	25	26	27	28	29
C_2H_4	1	12	13	14	..	24	25	26	27	..	..
C_2H_2	1	12	13	..	..	24	25	..	..	..	..

decreasing
⟶

The conclusion reached in this study is that under the influence of the canal rays, the hydrocarbons were converted into all possible decomposition products, including all kinds of radicals, down to the elements themselves. Furthermore, synthesis of all the known hydrocarbons was observed, including those which do not exist in free state, the synthetic products being built from the decomposition products present.

Many other striking examples could be cited, but the interested reader is referred to the special literature as it is beyond the scope of this book to delve further into this useful subject here.

4. Surface reactions

Our understanding of the mechanism of chemical action, on solid surfaces in catalytic reactions, has been elucidated, to a considerable extent, by the pioneering work of Irwing Langmuir.

Langmuir[1] studied wires, heated in various gases and found that hydrogen was dissociated into its atoms above 2100°K,* the dissociation, at low pressures, following the law of mass action, which was shown by the fact that the volume of the dissociation product was about twice the volume of the original gas. Consequently, the reaction is:

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[6] Eisenhut and Konrad: *Bunsen Society Meeting, Heidelberg, 1930.* Spectroscopy and Molecular Structure, p. 90. *Z. Electrochem.*, **36**, 644 (1930).

[1] Langmuir: *J. Am. Chem. Soc.*, **34**, 860 (1912).

* K = degrees Kelvin.

$$H_2 \rightarrow 2H + 130{,}000 \text{ cal.}$$

At pressures as low as 0.001–0.020 mm, the hydrogen, in contact with a tungsten wire, heated to a temperature of about 1300–2500° K, condensed on the wall of the glass vessel, and especially so when the vessel was cooled in liquid air. If the wire was cooled and the liquid air removed, molecular hydrogen was set free which did not again condense on the glass wall by renewed cooling to the temperature of liquid air. Using platinum and palladium wires, these phenomena were much more pronounced.[2]

The hydrogen, adsorbed by the glass surface, was active hydrogen and reacted, at room temperature, with oxygen and reducible substances, and it also dissolved in metals such as platinum.[3] This reactive hydrogen was considered to be in the atomic form.

Langmuir[4] also heated a tungsten filament in oxygen atmosphere at about 1200° K and a pressure of 100 bars.* The yellow tungsten oxide, WO_3, was formed and distilled off again as fast as it was formed, leaving a clean, bright surface.

When the tungsten filament was heated to 3300° K at a pressure of a few bars, it was shown that about half of all the oxygen molecules which struck the filament reacted with it to form WO_3, which distilled onto the bulb, and at least one half of the tungsten surface was covered with oxygen.

If the tungsten filament was heated to 1500° K or higher in pure, dry hydrogen at low pressure, the hydrogen was gradually dissociated into atoms, and the atomic hydrogen was adsorbed by the glass wall, where it reacted with any WO_3 which previously had been distilled onto the bulb.

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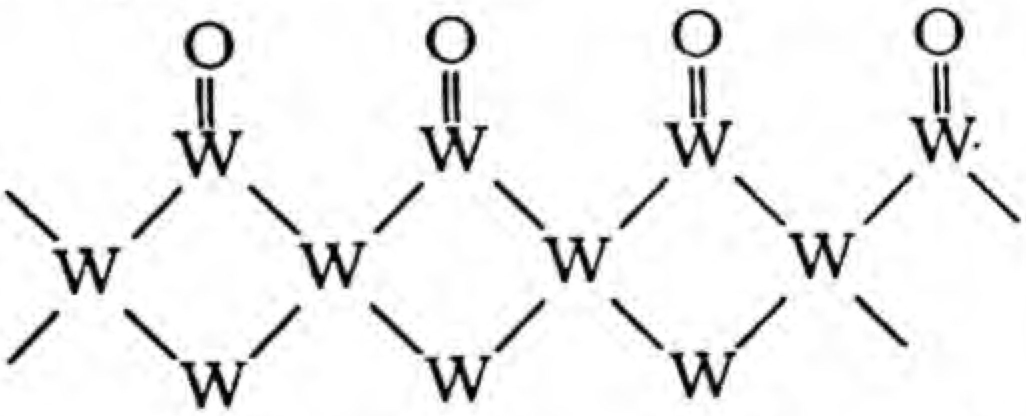
[2] Langmuir: *J. Am. Chem. Soc.*, **34**, 1310 (1912).
[3] Langmuir: *Ibid.*, **37**, 417 (1915).
[4] Langmuir: *Gen. Elec. Rev.*, July, 1922, p. 445.
* 1 bar = 0.1 mm pressure.

However, if minute traces of oxygen were admitted with the hydrogen, and the filament was heated to 1500°K, the oxygen reacted with the tungsten to form WO_3, and during this reaction, the dissociation of the hydrogen into atoms was prevented until all the oxygen was used up to form WO_3. The interesting feature is that under these conditions, the oxygen film, on the tungsten surface, does not react with the hydrogen to form water even at 1500°K. When passing methane through the bulb under conditions similar to the above, it decomposes into hydrogen and carbon; but if oxygen is mixed with the methane, this decomposition does not take place before all the oxygen is used up in formation of WO_3.

Langmuir concluded that the stable oxygen films, on the tungsten surface, consisted of a combination between individual oxygen atoms and the tungsten atoms, without an oxide of tungsten being formed by this part of the oxygen; but the oxygen atoms were considered to be held to the surface by four pairs of electrons (as to C in CO_2). This provides chemical saturation for the oxygen atoms, but not for the tungsten atoms which are held by strong forces to the underlying tungsten atoms:



Oxygen forms a similar film on carbon. Carbon monoxide, hydrogen, cyanogen, hydrogen sulfide, phosphine, and arsine form stable films on platinum, and Langmuir concludes that it is probable that all substances that have a poisoning effect on catalytic surfaces form films of this kind.

In a later paper, Langmuir[5] summarizes his observations.

The fraction of all the oxygen molecules that strike the surface of the tungsten filament, to form an oxide, was calculated as follows:

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[5] Langmuir: *J. Chem. Soc.*, April, 1940, p. 511.

$$\mu = \frac{p}{(2\pi m\kappa T)^{1/2}} \qquad \text{I}$$

where μ is the rate of arrival of the gas molecules, expressed in molecules $cm^{-2}\ sec^{-1}$, p is the pressure, T the absolute temperature, m the mass of the molecule, and κ a constant. By inserting numerical values we obtain:

$$\mu = 2.65 \cdot 10^{19} p(MT)^{-1/2} \qquad \text{II}$$

where M is the molecular weight of the gas and p is pressure in baryes (app. 0.01 mm of mercury). The fraction of all the impinging molecules, which react on striking the filament, ϵ is calculated by observing the rate of clean-up of the gas and comparing this figure with the data calculated from equation II. For filament temperatures from 1200 to 2000°K, the value of ϵ is given by

$$\log_{10}\epsilon = 1.76 - 5940/T \qquad \text{III}$$

For $T = 1500°K$, $\epsilon = 0.0063$. In experiments with a bulb of 5.5 liters, and a surface of the filament of 2.5 cm² the values of ϵ were:

T°K	t, sec	ϵ
1570	1500	0.0095
1710	270	0.0193
1870	175	0.038
2050	115	0.073
2210	54	0.118
2380	28	0.184
2520	16	0.253

The adsorbed film of oxygen consists of a single layer of firmly bound oxygen atoms which covers the surface almost completely; but these atoms do not react with each other, nor do they form WO_3. At very high temperatures, 2000°K or more, the adsorbed oxygen evaporates as free atoms, not as molecules. When oxygen molecules strike the surface, already covered with adsorbed oxygen, they condense on the surface to form a second layer of oxygen, probably as atoms, which are held by forces similar to those that hold the two oxygen atoms in peroxides together. These forces are much weaker than those which hold the mono-layer, and oxygen held this way evaporates above 1200°K. Each atom, in the second layer, moves freely over the surface until one of three possibilities occurs:

(1) The atom evaporates.

(2) The atom reacts with two oxygen atoms in the first layer, and with an underlying tungsten atom to form WO_3, which evaporates, leaving a hole in the first adsorbed layer.

(3) The atom drops from the second layer into any of the holes formed in the first layer and thus provides the mechanism by which the oxygen content of the first layer is held constant.

The amount of oxygen, in the second layer, is proportional to the oxygen pressure.

In studying the electron emission from tungsten filaments, Langmuir [6] found that the electron emission (at 1500°K) is about 100,000 times greater from a tungsten filament, containing one per cent of thorium oxide, than from a filament of pure tungsten. The thorium is here present as a single layer of atoms on the surface.

Langmuir [7] also studied the reaction: $2CO + O_2 = 2CO_2$, in contact with a platinum surface. The mechanism of this reaction is as follows:

(a) Every oxygen molecule, which strikes a clean platinum surface, condenses on the surface in the form of single atoms combined with separate platinum atoms. Every molecule of CO which strikes an adsorbed oxygen atom reacts with it to form CO_2.

(b) When CO molecules strike a clean platinum surface, they condense and are held by chemical union of the carbon atom to two platinum atoms. The CO molecules evaporate already at 500°K. This film of CO is very inert to oxygen.

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[6] Langmuir: *Phys. Rev.*, **22**, 357 (1923).

[7] Langmuir: *Trans. Faraday Soc.*, **17**, 1 (1921).

(c) At low temperatures (500–600°K), the surface is nearly completely covered with a film of CO, and the reaction is very slow.

(d) At high temperatures (above 1000°K), the surface is nearly covered with oxygen. If the oxygen is in excess, the rate of reaction depends on the rate at which the CO strikes the surface. If the CO is in excess, the surface is almost bare, and the reaction velocity depends on the rate at which the oxygen strikes the surface.

Studying the reaction $2H_2 + O_2 = 2H_2O$, using platinum as a catalyst, the deductions were similar to those just discussed for CO and oxygen, the hydrogen taking the place of the CO. At low temperatures (300–600°K), the rate of reaction depends on the previous treatment of the platinum, whereas at temperatures of 700–1900°K, the reaction is not sensitive in this respect. The experiments indicate that every collision between a hydrogen molecule and an adsorbed oxygen atom results in combination. When the platinum is conditioned for it, adsorbed hydrogen can react with oxygen molecules.

The surfaces of iron catalysts have been studied extensively. Wyckoff and Crittenden[8] studied a series of such catalysts, the composition of which was close to that of magnetite, Fe_3O_4. Different surfaces were prepared by adding to the iron oxide Al_2O_3, alone or with a small amount of K_2O. The degree of conversion of a mixture of hydrogen and nitrogen into ammonia, at 100 atmospheres and 450°C, and 5000 space velocity, was measured and reported as follows (as activity of the catalyst):

		Conversion %
Medium	=	**3–5**
Good	=	**5–6**
Very good	=	**6–10**
Extra good	=	**10–13**
Excellent	=	**13–15**
Equilibrium	=	**16.43**

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[8] **Wyckoff and Crittenden:** *J. Am. Chem. Soc.*, **47**, **2866 (1925).**

Chemical analysis and activity measurements gave the following results:

			Ferrous iron				
Catalyst No.	Total iron	Free iron	Ferrous iron	Ferric iron	K_2O	Al_2O_3	Activity
909	72.68	2.86	18.17	0.352	...	....	Medium
918*	72.84	2.37	25.03	0.551	...	....	Good
926	75.27	2.64	31.66	0.771	...	....	Medium
928	75.24	3.34	40.49	1.276	...	....	Medium
954	65.21	0.83	24.95	0.632	...	10.12	Very good
955	67.64	0.78	30.51	0.890	...	7.95	Good
922	71.99	0.89	24.55	0.533	0.26	1.05	Excellent
435	72.20	...	....	....	0.25	0.80	Excellent
421**	71.85	...	....	....	0.43	2.07	Extra good
660*	69.45	0.94	25.35	0.587	0.94	3.02	Excellent
940	69.15	...	....	....	2.16	2.95	Excellent
952A	62.98	0.41	20.16	0.475	5.81	7.75	Very good

* Red-heated.

** Contained 0.67% ZrO_2 as extra material.

It is noteworthy that the catalysts, which caused the highest conversion, contained both K_2O and Al_2O_3. Emmet and Brunauer [9] have found that CO_2 is chemisorbed at $-78°C$ only on those iron catalysts which contain alkali as a promoter. Also, on the same type of catalysts, the amount of chemisorbed CO at $-183°C$ (instantaneously) was smaller than on catalysts without the promoter; and the sum of the chemisorbed CO_2 and CO, on catalysts containing both Al_2O_3 and K_2O, appeared to be equal to the amount required to form a monomolecular layer over the entire catalyst. The results indicated that the CO_2 was adsorbed by the alkali on the surface of the catalyst, and the CO by the surface iron atoms. On the basis of these data, it was calculated that an ammonia catalyst of iron, containing 1.39 per cent Al_2O_3 and 1.59 per cent K_2O, had its surface covered with the molecules of the promoters to an extent of 60 to 75 per cent. One catalyst, containing 10.2 per cent Al_2O_3 and no alkali, had 50 per cent of its surface covered with the promoter.[10]

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[9] Emmett and Brunauer: *J. Am. Chem. Soc.*, **59**, 310 (1937).

[10] Emmett, P. H.: *Physical Adsorption in the Study of the Catalyst Surface,* Twelfth Report of the Committee on Catalysis, National Research Council, New York, John Wiley & Sons, Inc., 1940.

These results are in good agreement with Langmuir's observation with respect to the electron emission of a tungsten filament, containing a little thorium oxide.

The adsorption of nitrogen, at −90.1 °K, on different synthetic ammonia catalysts, was estimated by Emmett et al.,[10, 11] the figures indicating cubic centimeters of gas corresponding to a monomolecular layer on one gram of catalyst.

Substance	Adsorption of nitrogen, cc/g
Unpromoted Fe catalyst 973I	0.12
Unpromoted Fe catalyst 973II	0.27
Fe–Al_2O_3 catalyst 954	2.78
Fe–Al_2O_3 catalyst 424	2.09
Fe–Al_2O_3–K_2O catalyst 931	0.76
Fe–Al_2O_3 catalyst 958	0.55
Fe–K_2O catalyst 930	0.12
Fused Cu catalyst	0.05
Commercial Cu catalyst	0.10
Cr_2O_3 gel	50.5
Cr_2O_3 glowed	6.14
Silica gel	127.0

In the case of the iron catalysts, Brunauer and Emmett [12] have shown that the nitrogen is adsorbed on the iron atoms. The higher adsorption on the Fe-Al_2O_3 catalyst is probably due to the fact that the iron, in this case, was of finer crystals than the non-promoted catalysts.

Studies, on the exchange reaction between ethylene and deuterium[13, 14] over nickel as catalyst ($C_2H_4 + D_2 \rightleftarrows C_2H_3D + HD$), between 60 and 207 °C, showed that the reaction $H_2 + D_2 \rightleftarrows 2HD$ is completely inhibited up to 160 °C, due to strong adsorption of ethylene below this temperature. Above 160 °C, the ethylene is desorbed by the nickel. From this study, it was concluded that the interatomic distance of the catalyst atoms is an important factor in determining the activity of the catalyst. For the nickel catalyst, the length of the Ni-Ni linkage—the closest packing—

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[11] Brunauer, Emmett and Teller: *J. Am. Chem. Soc.*, **60**, 309 (1938).

[12] Brunauer, and Emmett: *Ibid.*, **62**, 1732 (1940).

[13] Twigg and Rideal: *Proc. Roy. Soc. (London)*, **A 171**, 55 (1939).

[14] Twigg and Rideal: *Trans. Faraday Soc.*, **36**, 53 (1940).

is 2.47 Å. In general, catalysts, which are active in hydrogenation, have interatomic distances between 2.47 and 2.54 Å (Fe, Ni, Co, Cu) and 2.7 and 2.8 Å (Pt, Pd). The reason for this is that such catalysts permit fitting of the $-C=C-$ structure to the nickel structure (Ni — C linkage 1.82 Å; C — C linkage 1.52 Å). The (110) plane of the nickel, which is the one of least density, is catalytically active, whereas the (100) plane is inactive.

In a comprehensive study on the catalytic activity, crystal structure, and the adsorptive properties of evaporated metal films, produced by condensation of the vapors of the metals on glass, both oriented and unoriented films were produced.[15] In completely oriented nickel films, the least dense of the planes, the (110) plane, was lying parallel to the backing and the two remaining axes showed random distribution. Iron films also were oriented with their least dense plane, the (111) plane, parallel to the backing. By low-pressure adsorption of hydrogen, at room temperature, and of CO, at liquid air temperature, it was revealed that the oriented, gas-evaporated nickel films have twice the available surface per gram of randomly oriented high-vacuum films and ten times their activity. The adsorption of hydrogen was, in all cases, immeasurably fast. By poisoning experiments with CO and O_2, it was found that loss of activity, decrease of hydrogen adsorption, and the amount of poison were proportional.

Taylor,[16] who has contributed considerably to the elucidation of the general physical chemistry of catalytic surfaces, conceives the catalyst surface as consisting of unsaturated atoms, more or less loosely held to the underlying lattice structure, such peak atoms being haphazardly distributed on the surface and having a varied number of free valences, depending on their relative position to other metal atoms:

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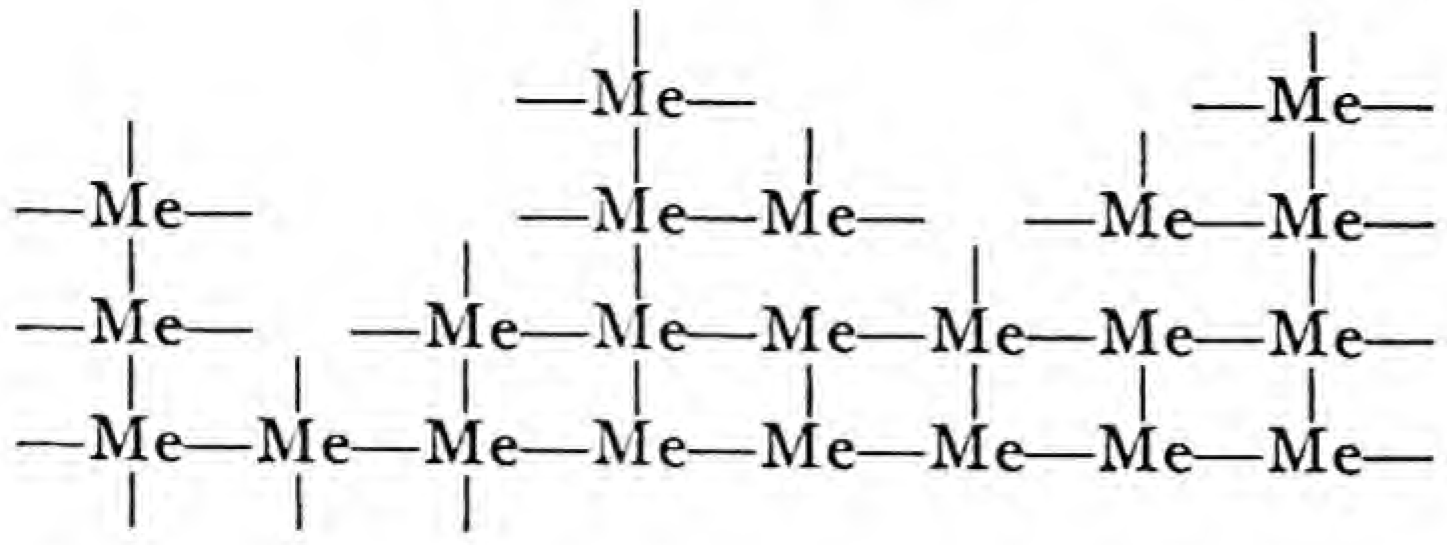
[15] Beeck, Smith and Wheeler: *Proc. Roy. Soc. (London)*, **A 177**, 62 (1940).

[16] Taylor: *J. Phys. Chem.*, **30**, 145 (1926); *ibid.*, **31**, 277 (1927); *Proc. Roy. Soc.*, **A 108**, 105 (1925); *Twelfth Report of the Committee on Catalysis*, National Research Council, New York, John Wiley & Sons, Inc., 1940, p. 41.



Such peak atoms, with unsaturated valence forces, are considered to be the seat of the catalytic activity of the surface and called active centers. This conception of a haphazardly uneven surface has its counterpart in etched metal surfaces.

The surface of a crystal is chemically unsaturated and, consequently, is the seat of a definite surface energy, but the rigidity of the surface atoms prevents the formation of surface-tension effects. However, the surface of a solid also tends to reduce itself, this being accomplished by adsorption onto the surface of molecules or atoms from the gaseous or liquid phase with which the solid surface is in contact.

The extent of the surface reaction, from a kinetic point of view, is illustrated in the following table by Hurt[17] who presents data showing the relative importance of mass transfer and surface reaction rates for average, plant-scale operating conditions:

Reaction	% of total reaction time for mass transfer	for surface reaction
$CO + H_2O \rightarrow H_2 + CO_2$	60	40
$N_2 + 3H_2 \rightarrow 2NH_3$	15*	85*
$CO + 2H_2 \rightarrow CH_3OH$	20*	80*
$CO + 3H_2 \rightarrow CH_4 + H_2O$	50	50
$2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O$	80	20
$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	160**	—

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[17] Hurt: *Ind. Eng. Chem.*, 35, 522 (1943).

* These reactions are known to be reversibly poisoned by the reaction products. However, insufficient data for evaluating the poisoning coefficients were available, and omission of this factor may have appreciably affected the results shown.

** This indicates that the oxidation of ammonia on platinum is a chain reaction, extending into the gas phase.

GENERAL REFERENCES

Brunauer, S.: *Physical Adsorption,* Princeton, Princeton University Press, 1943. **Buzag, A. V.:** *Colloid Systems.* A Survey of the Phenomena of Modern Colloid Physics and Chemistry, London, The Technical Press, Ltd., 1937.

5. Positive catalysis

Positive catalysts are substances or mixtures of substances which, when present in a reaction system, accelerate the velocity of a chemical reaction, without appearing in the end product.

In its simplest form, positive catalysis is illustrated by the following general reaction mechanism, where the reacting molecules A and B combine only in the presence of the catalyst C:

$$\text{I.}\quad A + C + B \rightarrow AC + B$$

$$\text{II.}\quad AC + B \rightarrow AB + C$$

Whereas molecule B does not react directly or it reacts only slowly with molecule A, the formation of molecule AC produces a combination in which A has greater affinity for B than it has for C, which is regenerated.

In reversible processes, a positive catalyst acts in bringing about equilibrium faster than without a catalyst, but the catalyst does not change the equilibrium point. Consequently, the two opposing reactions are accelerated to the same extent by the catalyst, which, in fact, is the case with both homogeneous and heterogeneous catalytic reactions.[1]

Positive catalysts may also permit a chemical reaction to take place at lower temperature than it would proceed without the presence of a catalyst.

6. Negative catalysis

Negative catalysts are substances or mixtures of substances which decrease the velocity of a chemical reaction, but do not bring the reaction to cessation. Negative catalysis has not been studied to nearly the same extent as positive catalysis, although negative catalytic reactions are of very great importance. For detailed study, the extensive reference work of Kenneth C. Baily[1] is recommended.

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[1] Brönsted, J. N.: *Physical Chemistry,* London, William Heinemann, Ltd., 1937, p. 247.

The industrial importance of retardation of chemical reactions is well known in such problems as oxidation (rancidity) of oils and fats, anti-oxidants for rubber, anti-knock compounds for motor fuels, prevention of metallic corrosion, retardation of setting of cement and plaster, etc.

The presence of small quantities of water greatly decreases the velocity of reactions which take place in an anhydrous medium, such as esterification of acids, alcoholysis, decomposition of oxalic acid in anhydrous sulfuric acid,[2] etc.

The formation of Grignard's organo-magnesium compounds is retarded by the presence, in the ether or in the alkyl compounds, of anisole, ethyl acetate, chloroform, or carbon bisulfide.[3] The formation of hydrochloric acid is retarded by oxygen.[4] A classical example of negative catalysis is Bigelow's[5] study of the oxidation of sulfites by atmospheric oxygen; he found that compounds, containing hydroxyl groups, retard the formation of sulfate.

Negative catalysis has been explained in several ways, the more important of these appearing to be:

(a) Slow formation of the Brönsted critical compound (see page 9), too great stability of an intermediate catalyst compound (see page 10), or retardation in desorption of the reaction products (see page 36).

(b) The intermediate compound regenerates both the negative catalyst and the reactant:

$$A + \underset{\text{catalyst}}{C} + B \rightarrow AC + B$$

$$AC + B \rightarrow A + \underset{\text{catalyst}}{C} + B$$

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[1] Baily, K. C.: *The Retardation of Chemical Reactions,* London, Edward Arnold & Co., 1937.

[2] Taylor: *J. Phys. Chem.,* **27**, 322 (1923).

[3] Sabatier, P.: *La Catalyse en Chimie Organique,* Paris, 1920. (Sabatier and Reid: *Catalysis in Organic Chemistry,* New York, D. Van Nostrand Co., 1923.)

[4] Green, S. J.: *Industrial Catalysis,* New York, Macmillan Co., 1928.

[5] Bigelow: *Z. physik. Chem.,* **26**, 493 (1898).

(c) Catalytic side reactions or decomposition [6]

(d) Breaking of a chain reaction.[7, 8] Chain reactions are mostly very sensitive to negative catalysis.

The rate of the hydrolytic decomposition, at 50°C, of bromo-succinic acid [9] is directly proportional to the concentration of the unchanged bromo-succinic acid, $\left(\frac{a - x}{v}\right)$, and inversely proportional to the concentration of the hydrobromic acid formed, $\left(\frac{x}{v}\right)$, which acts as a negative catalyst, the rate of the reaction being:

$$\frac{dx}{dt} = k\frac{a - x}{x}$$

Strong acids retard this reaction, which otherwise is auto-catalytic. It is undoubtedly quite general in homogeneous catalysis that the reaction products cause negative catalysis.[10]

Midgley and Boyd [11] found that detonation, in a gasoline engine, can be either retarded or induced by the presence of very small amounts of certain materials in the combustible mixture. These substances may be dissolved or suspended in the fuel, or they may be admitted to the combustion chamber in some other way. Some examples are as follows (*Ind. Eng. Chem.*, **14**, 894, 1922):

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[6] Robertson: *Proc. Nat. Acad. Sc. U.S.A.*, **13**, 192 (1927).

[7] Christiansen: *J. Phys. Chem.*, **28**, 145 (1924).

[8] Bäckström: *J. Am. Chem. Soc.*, **49**, 1460 (1929); *Trans. Faraday Soc.*, **24**, 601 (1928).

[9] Müller: *Z. physik. Chem.*, **41**, 483 (1902).

[10] Roginskii: *J. Phys. Chem. (U.S.S.R.)*, **13**, 1787 (1939).

[11] Midgley and Boyd: *Ind. Eng. Chem.*, **14**, 589, 819, 894 (1922).

Element	Typical compound	Effect on reaction velocity of combustion	Approximate number of mols of theoretical fuel-air mixture in which 1 mol exerts an effect on original detonation of a given magnitude
Iodine	Element	Retards	
Bromine	Element	Accelerates	
Oxygen	Element	Accelerates	
Oxygen	$C_2H_5NO_3$ or $C_2H_5NO_2$	Accelerates	
Nitrogen	$C_6H_5NO_2$	Retards	
Selenium	$(C_2H_5)_2Se$	Retards	11,750
Tellurium	$(C_2H_5)_2Te$	Retards	50,000
Tin	$(C_2H_5)_4Sn$	Retards	7,100
Lead	$(C_2H_5)_4Pb$	Retards	215,000

Midgley[12] used the following formula for calculating the velocity constant (K) of the treated fuels:

$$K = K_0 - 0.173 \times 10^{-7} \cdot \log_e(C + 1)$$

where K_0 is the reaction velocity constant of the original fuel and C is the concentration of tetraethyl lead in cc per gallon of fuel.

Concentration of lead tetraethyl, cc per gallon	K
0	3.25×10^{-7}
1	3.17×10^{-7}
2	3.075×10^{-7}
4	2.97×10^{-7}
8	2.86×10^{-7}
16	2.76×10^{-7}

GENERAL REFERENCE

Dhar: *Trans. Faraday Soc.*, **24**, 565, 567 (1928).

7. Autocatalysis

In this type of reaction, one of the reaction products acts as catalyst. This being the case, there is no catalyst present at the beginning of the reaction.

If in the reaction of the substances A and B, A′ is a catalyst, and the reaction is autocatalytically producing one molecule of A′ for each molecule of A and B which react, then:[1]

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[12] Midgley: *Ind. Eng. Chem.*, **15**, 421 (1923).

$$\begin{array}{ll} 1. & 2A \rightarrow A + \underset{\text{active}}{A'} \\ 2. & A + A' + B \rightarrow A + A'B \\ 3. & A'B + A \rightarrow A' + AB \\ \hline 4. & 2A + B \rightarrow AB + \underset{\text{active}}{A'} \end{array}$$

The rate of such a reaction is:

$$\frac{dx}{dt} = k(a + x)(b - x)$$

x being the number of moles of A and B reacting after t minutes, and k a constant; from this equation k is calculated by integration:

$$k = \frac{1}{t(a + b)} \ln \frac{b(a + x)}{a(b - x)}$$

When linseed oil is exposed to air in thin films, it undergoes slow autoxidation and can absorb more than twenty per cent of its weight of oxygen. Genthe[2, 3] found that the increase in weight with time follows the equation:

$$\frac{dx}{dt} = k(a - x)(b + x)$$

where a is the initial concentration of linseed oil; b the initial concentration of the autocatalyst; t = time, x = concentration of oxidized linseed oil at time t, and k is a constant.*

Boiled linseed oil is not readily oxidized by air because the autocatalyst is destroyed by boiling, but if the boiled oil is reblown, it autoxidizes again. On addition of oil-soluble salts of Mn, Zn, Co, V and U, the drying takes substantially less time.

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[1] Rice, F. O.: *The Mechanism of Homogeneous Organic Reactions from the Physico-Chemical Standpoint,* New York, Reinhold Publishing Corp., 1928.

[2] Genthe: *Z. angew. Chem.,* 19, 2087 (1906).

[3] Rideal and Taylor: *Catalysis in Theory and Practice,* London, Macmillan and Co., Ltd., 1919, p. 150.

* According to Stephens autoxidations may be due to impurities [*Ind. Eng. Chem.,* **24,** 919 (1932); *J. Am. Chem. Soc.,* **58,** 219 (1936)].

Slow coagulation, in the sensitive range of electrolyte concentration, proceeds autocatalytically, the rate being:

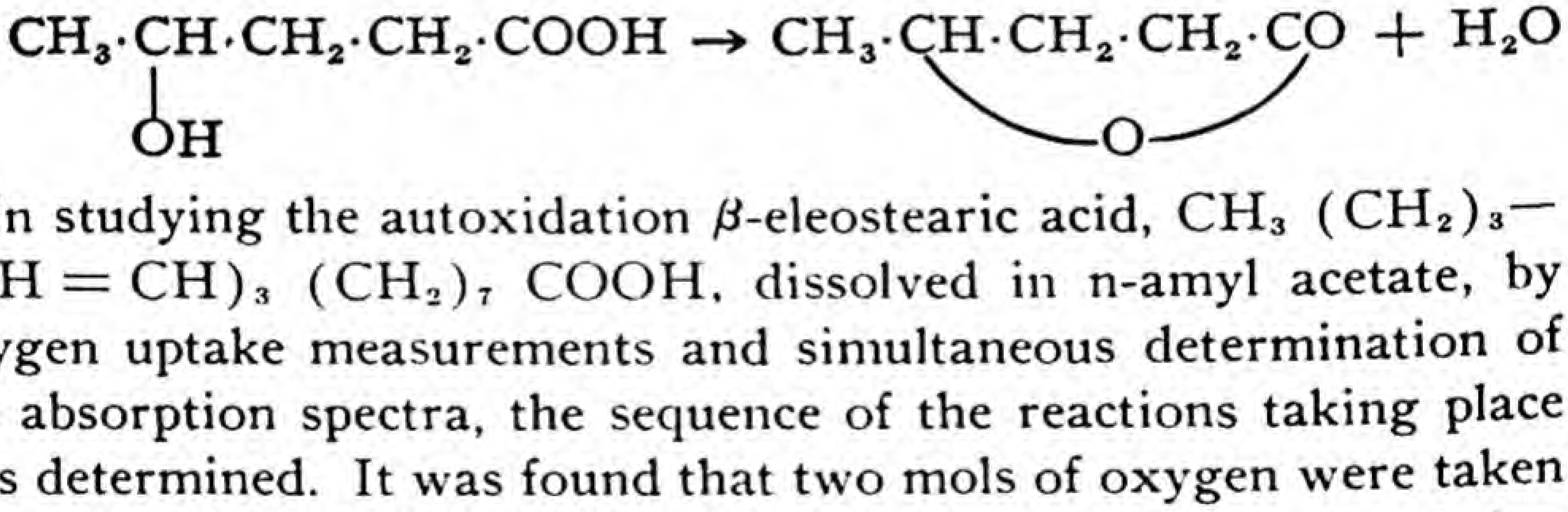
$$\frac{dx}{dt} = K(1 + bx)(1 - x)$$

where K and b are constants, x is the change in time t, and b is equal to dx/dt at a point of inflection of the x — t curve.

Green[4] calls attention to two commonly known, but illuminating autocatalytic reactions, viz.: (1) the hydrolysis of esters which is catalyzed by the acid formed and thus, the catalytic action increases as the reaction proceeds; and (2) the lactone formation from hydroxy acids, being catalyzed by hydrogen ions, the catalytic action decreasing as the reaction proceeds:

1. $CH_3COO{\cdot}C_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$

2.



$$CH_3{\cdot}\underset{OH}{CH}{\cdot}CH_2{\cdot}CH_2{\cdot}COOH \rightarrow CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO + H_2O$$

In studying the autoxidation β-eleostearic acid, $CH_3\ (CH_2)_3$— $(CH = CH)_3\ (CH_2)_7\ COOH$, dissolved in n-amyl acetate, by oxygen uptake measurements and simultaneous determination of the absorption spectra, the sequence of the reactions taking place was determined. It was found that two mols of oxygen were taken up per mol of β-eleostearic acid, this amount of oxygen being recovered in a dibasic acid which is considered as probably being a dimer of the original acid. Three fourths of the absorbed oxygen in this product is removed by means of alkali.[5]

Another important autocatalytic process is the autoxidation of ascorbic acid at various acidities. If sufficient cyanide or thiocyanate is present to suppress the catalytic action of metals, both the monovalent and bivalent ion of the acid participate in the reaction. With oxygen at atmospheric pressure, the divalent ion reacts 10^5 times faster than the monovalent ion. However, if the partial oxygen pressure is reduced one fifth, the reaction rate of the divalent ion sinks in proportion to the oxygen concentration, but not the reaction rate of the monovalent ion. If the catalytic action of the metals is not suppressed by cyanide or thiocyanate, the reaction rate of the monovalent ion is proportional to the oxygen concentration. It was also found that only the monovalent ion of 1-ascorbic acid is the substrate of copper catalysis, a concentration of 2×10^{-5} mol per liter of copper increased the reaction rate of the monovalent ascorbic ion by a factor of 10^4.[6]

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[4] Green, S. J.: *Industrial Catalysis*, New York, Macmillan and Co., 1928.

[5] Brauer and Steadman: *J. Am. Chem. Soc.*, **66**, 563 (1944).

In acid-base catalysis, both the acid and the base must be present before the reaction takes place. If the reacting substance itself can react as a base of substantial concentration, the addition of acid will make the reaction take place, and conversely, if the reacting substance itself can react as an acid, the addition of a base will make the reaction take place. In this case, a catalyst is required to initiate a chemical reaction. Such catalysis is undoubtedly extremely important in living organisms in which amphoteric electrolytes are in abundance. Also in the case of accumulation of mineral constituents in root cells in the soil solution and in algae, in ponds, autocatalysis undoubtedly plays a considerable part.

Water, being both an acid and a base, is an important autocatalyst, although it is very little dissociated.

GENERAL REFERENCE

Desal: *Trans. Faraday Soc.*, **24**, 181 (1928).

8. Chain reactions

These processes are exothermic, and the end products are formed with so much energy that fresh reactant molecules are activated, and the same series of reactions is repeated. In energy or physical chains, the activation is due to direct transfer of energy from the reaction product to the initial substance (predominant at high temperatures and in strongly exothermic processes), and in material or chemical chains, the activation is due to formation of reactive intermediate substances rich in energy, e.g., Cl-atoms, OH-radicals, etc. (predominant at not too high temperatures and in stationary chains). All chain reactions involve some particular process which breaks the chain when a stationary state is attained, as otherwise, explosion will occur. Schwab[1, 2] gives the following illustration of a chain reaction mechanism:

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[6] Weissberger et al.: *J. Am. Chem. Soc.*, **65**, 1934 (1943); **66**, 700 (1944).

1. $A \rightarrow A'$ *
2. $A' \rightarrow A$
3. $A' + B \rightarrow AB'$
4. $A + AB' \rightarrow A' + AB$ (chain propagating)
5. $AB' + C \rightarrow AB + C'$ (chain breaking)

In this scheme, A, B, and C are the initial reactants; A′ and AB′ are energy-rich intermediate states; AB and C′ are the end products. When the reaction has reached a stationary state, the intermediate products are removed as fast as they are formed, and we have the following equilibria and rates:

$$[A]_{k_1} + [A][AB']_{k_4} = [A']_{k_2} + [A'][B]_{k_3}$$

$$[A'][B]_{k_3} = [A][AB']_{k_4} + [AB'][C]_{k_5}$$

$$+\frac{d[AB]}{dt} = \frac{[A]^2[B]_{k_1 k_3 k_4} + [A][B][C]_{k_a}}{[A]_{k_b} + [B]_{k_c} + [B][C]_{k_d}}$$

According to Hinshelwood[3] chain reactions may be recognized by the following characteristics:

1. Photochemical reactions: Abnormally great quantum yield.
2. Thermal reactions: Retardation of the change by a decrease

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[1] Schwab, G. M., H. P. Taylor and R. Spence: *Catalysis from the Standpoint of Chemical Kinetics,* New York, D. Van Nostrand Co., Inc., 1937.

[2] Bodenstein, Podelt, and Schumacher: *Z. physik. Chem. B,* 5, 209 (1929).

* The apostrophe indicates an energy-rich molecule.

[3] Hinshelwood, C. N.: *The Kinetics of Chemical Change in Gaseous Systems,* Oxford, Clarenden Press, 1933, p. 271.

in the dimension of the vessel, allowing a smaller path for the chains to traverse before reaching the wall.

3. Acceleration of the reaction, in some instances, by the presence of an inert gas [the inverse of (2)].
4. Abnormal influence of the concentration of the reacting substances on the rate, due to the fact that the concentrations affect the number of chains starting in unit time and also the successfulness of their propagation.
5. A rate of reaction considerably greater than may be expected from a knowledge of the heat of activation and the collision number.
6. Sensitivity of the reaction to inhibitors.
7. In certain examples, the appearance of the remarkable phenomenon of abrupt transitions from negligibly slow reaction to explosion.

Which of these characteristics appear in a given reaction depends on the length of the chain and the manner of its starting and stopping. As a rule, all the characteristics are not shown by any one reaction.

Bodenstein[4] published the first conception of a chain mechanism, in 1913, and the idea was later pursued by Nernst,[5] Christiansen,[6] Hinshelwood,[3, 7] Haber,[8] Semenov,[9, 10] Bursian and Sorokin,[11] and Pease.[12] Semenov's treatise,[9] on the subject of chain mechanisms, is very elaborate, and readers are referred to this standard work.

The length of a non-branching chain[8, 9] is calculated as follows. The conditions, for a chain reaction, are that an initially active center y, entering a chain reaction, can create a similar active center y and thus continue the chain. If α is the probability that the center y, in entering the reaction, will create a new center continuing the chain, then

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[4] Bodenstein: *Z. physik. Chem.*, **85**, 329 (1913).

[5] Nernst: *Z. Elektrochem.*, **24**, 335 (1916).

[6] Christiansen and Kramer: *Z. physik. Chem.*, **104**, 451 (1923).

[7] Hinshelwood et al.: *Proc. Roy. Soc. (London)*, **118**, 170 (1928); *ibid.*, **119**, 591 (1928); *ibid.*, **122**, 610 (1928); *Trans. Faraday Soc.*, **24**, 559 (1928).

[8] Haber and Willstätter: *Ber.*, **64**, 2844 (1931).

[9] Semenov, N.: *Chemical Kinetics and Chain Reactions*, Oxford, Clarenden Press, 1935.

[10] Semenov et al.: *Z. Physik.* **46**, 109 (1927); *ibid.*, **48**, 571 (1928); *Z. physik. Chem.*, **1B**, 192 (1928); *ibid.*, **2B**, 161 (1929).

[11] Bursian and Sorokin: *Z. physik. Chem.*, **12B**, 247 (1931).

[12] Pease: *J. Am. Chem. Soc.*, **51**, 1839 (1929).

$$1 - \alpha = \beta$$

is the probability that it will not create a new center and will be eliminated from the reaction, without prolonging the chain.

The probability that the chain will consist of s links, which requires that y should be regenerated s − 1 times, and that the sth active center should break the chain (i.e., it should react without regeneration), is given by

$$p_s = \alpha^{s-1}(1 - \alpha)$$

The average chain-length, ν, i.e., the number of reactions producing it, is then given by

$$\nu = \sum_{s=1}^{s=\infty} sp_s = \sum_{1}^{\infty} s\alpha^{s-1}(1 - \alpha) = \frac{1}{1 - \alpha} = \frac{1}{\beta}$$

where β is the probability that the chain is broken at a given link. The length of the chains varies from 0 to ∞, short chains predominating.

If the center perishes, without entering the reaction, and a secondary center is formed, as in the case of formation of hydrochloric acid from hydrogen and chlorine ($Cl + H_2 \rightarrow HCl + H$; $-H + Cl_2 \rightarrow HCl + Cl$; $-Cl + H_2 \rightarrow HCl + H$, etc.), then, if the probability that y will react is α, the probability for the chain to have s links will be

$$p_s = \alpha^s(1 - \alpha)$$

Consequently, the average length will be

$$\nu = \sum_{s=1}^{s=\infty} s\alpha^s(1 - \alpha) = \frac{\alpha}{1 - \alpha} = \frac{1 - \beta}{\beta}$$

The quantity $\frac{\alpha}{1-\alpha}$ is the average length of the straight chain, the length of the individual chains varying from 0 to ∞.

The branching of a chain [9] is the result of formation of two new centers, one of which may prolong the chain and the other begin a secondary or branched chain. The secondary chains can generate tertiary chains by further branching. The probability, that a chain will branch at a given link, is denoted by δ. β is the probability that the straight chain will break, as branching opposes breaking, the difference of the two probabilities, $\beta - \delta$, gives the probability for the breaking of the chain if branching is neglected. Thus, the total length of the branched chain, ν', is expressed by

$$\nu' = \frac{1}{\beta - \delta} = \frac{\nu}{1 - \nu\delta}$$

For the continuously branched chain $\delta = 1 - \beta$, thus:

$$\nu' = \frac{1}{\beta - \delta} = \frac{1}{2\beta - 1}$$

The velocities for the chain reactions are: [9]

(1) Non-branching chains. If n_o is the number of initial active centers generated in unit volume, the velocity of the chain reaction, v, (unit volume) will be:

$$v = n_o\nu = \frac{n_o}{1-\alpha} = \frac{n_o}{\beta}$$

However, when the chain reaction starts, this constant value is not reached immediately because time is required for the development of the chain. If the time, required for the formation of one link of the chain, is Δt, then the whole chain of average length ν is developed in a time $t = \nu\Delta t$.

(2) Branching chains. The velocity, v′, of this type of chain is given by:

$$v' = n_o\nu' = \frac{n_o\nu}{1 - \nu\delta}$$

and in the case of a continuously branched chain by:

$$v' = \frac{n_o}{2\beta - 1}$$

If $\beta - \delta < O$, the number of branchings is greater than the number of ruptures and the number of chains increases steadily, a case which corresponds to self-accelerated chemical processes such as explosions.

9. Induced reactions

In practically all cases of induced reactions, the primary reaction is exothermic and is likely to generate ions and electrons which are the activators.[1]

If mercuric chloride is boiled, in the dark, with oxalic acid, no mercurous chloride is formed unless a drop of potassium permanganate is added ($2HgCl_2 + H_2C_2O_4 \rightarrow 2HgCl + 2HCl + 2CO_2$). Evidently, the exothermic reaction between oxalic acid and potassium permanganate induces the reaction between oxalic acid and mercuric chloride.[1]

Frankenburger [2] terms as inductors substances which increase the velocity of a reaction and are used up in doing so. Induced oxidation is a phenomenon which was recognized very early by Schoenbein [3] who showed that in the case of many autoxidation processes, for an atom of oxygen consumed by the compound being oxidized, a molecule of oxygen was simultaneously transformed into a more active state. Oxygen, activated in this way, can react with more oxygen to form ozone and with water to form hydrogen peroxide, or oxidize other oxidizable substances not oxidized directly by atmospheric oxygen.

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[1] Dhar: *Trans. Faraday Soc.*, **24**, 566 (1928).

[2] Frankenburger, W.: *Katalytische Umsetzungen in homogenen und enzymatischen Systemen*, Leipzig, Akademische Verlagsgesellschaft M.B.H., 1937, pp. 6, 11, 241, 250, 276.

[3] Schoenbein: *J. prakt. Chem.*, **24**, 325 (1842); *ibid.*, **75**, 105 (1868).

10. Induction periods

According to Hinshelwood,[1] a great number of reactions, having the characteristics of chain reactions, start with an induction period the rate of change of which is almost nil, but at the end of the induction period, measurable reaction or explosion sets in. If the centers, from which branching chains can proceed, are initially poisoned and the poison is slowly removed by reaction with one of the reacting substances, the reaction will function at a certain point and it may then take place.

Induction periods may also be interpreted as being due to autocatalysis by an intermediary product, resulting from the reaction, or by the final reaction product. The induction period may also be caused by the actual time it takes for branching chains to develop.[1]

Akulov [3] gives the velocity of a chemical reaction as follows:

$$\frac{d\alpha}{dt} = k[\alpha + (d\alpha/dt)t]\ (1 - \alpha)$$

where α is the fraction of substance converted at time t and k is the reaction constant. This equation accounts for an induction period, and it is claimed that it agrees well with experimental data on different types of reactions.

An example of induction period is the catalytic decomposition of hydrogen peroxide in the presence of iron citrate: [2]

Cubic centimeters of citrate 0.1 molarity	$[\text{Citrate}^{---}]$ $[\text{Fe}^{+++}]$	Time for half-time reaction, minutes	Induction period, minutes	Duration of the reaction, minutes
0.0	0	61	0	61
0.063	0.0189	23	2 (?)	21
0.125	0.038	16	2 (?)	14
0.188	0.056	14	2 (?)	12
0.375	0.113	11	2 (?)	9

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[1] Hinshelwood, C. N.: *The Kinetics of Chemical Change in Gaseous Systems*, Oxford, Clarenden Press, 1933, p. 299.

[2] Mordechai, Bobtelsky, and Kirson: *Compt. rend.*, **208**, II, 1577 (1939).

[3] Akulov: *Compt. rend. acad. sci. U.S.S.R.*, **28**, 135 (1940); *Chem. Abstracts*, **35**, 2777 (1941).

Cubic centimeters of citrate 0.1 molarity	$[\text{Citrate}^{---}]$ $[\text{Fe}^{+++}]$	Time for half-time reaction, minutes	Induction period, minutes	Duration of the reaction, minutes
0.67	0.201	10	3 (?)	7
1.17	0.351	14	6	8
1.67	0.501	21	8	13
1.93	0.579	28	11	17
2.2	0.66	39	17	22
2.5	0.751	81	45	36
2.6	0.78	..	very long	..

In the thermal catalytic reaction between chlorine and ozone at 35 and 50°C, there is an induction period of about half an hour, before the reaction proceeds at its regular velocity.[4] Many other examples are known.

11. Promoters

A promoter is a substance, the addition of which to a catalyst increases its activity. Used alone, a promoter does not act catalytically. A promoter may also change the direction of the reaction, i.e., it may influence the selectivity of a catalyst.

Pioneers in this field are Bosch and Mittasch[1] and Ipatieff.[2] A classical example of promotion is offered in the synthesis of ammonia, where iron replaced osmium and uranium as catalysts. It was found that admixtures of other metals, as well as their oxides, to the iron catalyst improved both its activity and its life.

The fact that a promoter may have a catalytic action, different from that of the catalyst, has been shown by Ipatieff and Matov,[3] who used a nickel catalyst, promoted with alumina, for converting camphor into isocamphane. It was found that the hydrogenation of camphor ($C_{10}H_{16}O$), borneol ($C_{10}H_{17}OH$), and fenchene

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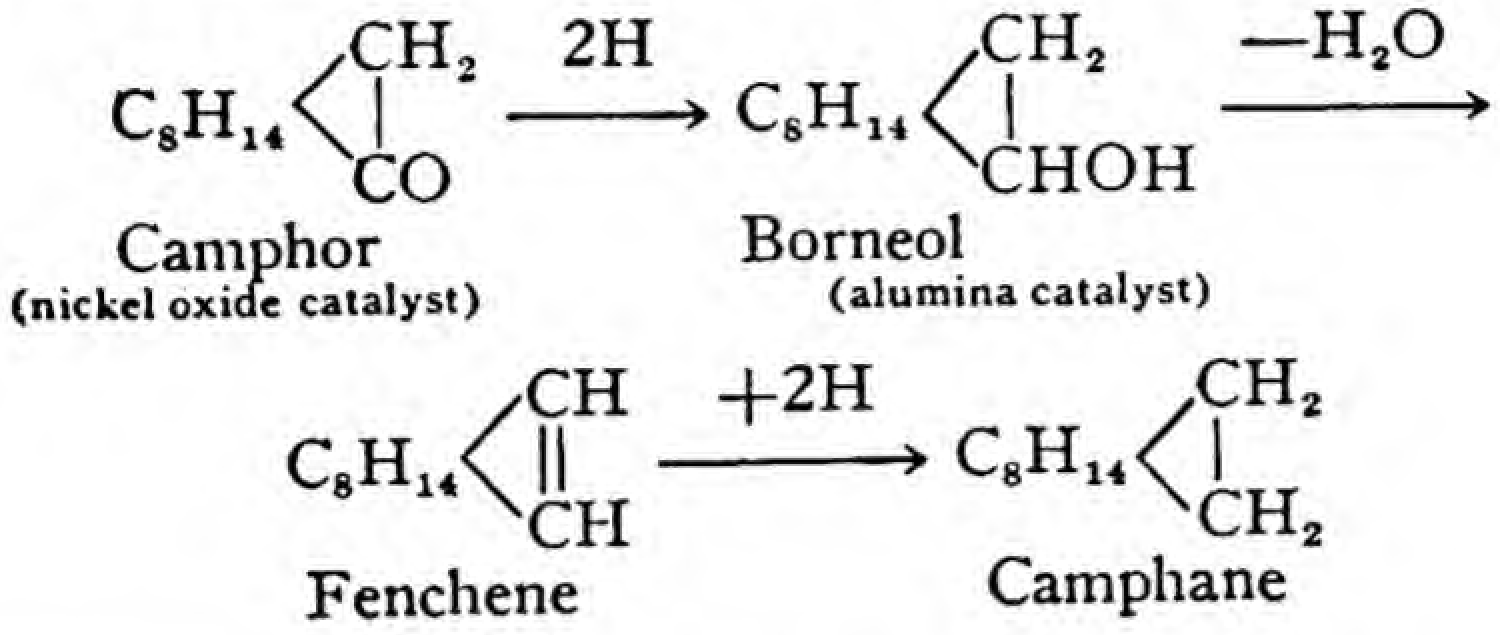
[4] Bodenstein, Podelt and Schumacher: *Z. physik. Chem.*, **B 5**, 209 (1929).

[1] Mittasch: *Ber.*, **59**, 13 (1926).

[2] Ipatieff: *Ibid.*, **45**, 3205 (1912).

[3] Ipatieff and Matov: *J. Russ. Phys. Chem. Soc.*, **44**, 1695 (1912); Ipatieff: *Catalytic Reactions at High Pressures and Temperatures*, New York, The Macmillan Company, 1937, p. 533.

($C_{10}H_{16}O$), in the presence of nickel oxide, does not begin under 360–400°C, and proceeds very slowly, with the formation of by-products. If, however, alumina is added, the hydrogenation proceeds readily at 190–200°C, producing almost quantitative yields of camphane ($C_{10}H_{18}$), fenchene ($C_{10}H_{16}$) and other compounds:



$$C_8H_{14}\left\langle\begin{matrix}CH_2\\|\\CO\end{matrix}\right. \xrightarrow{2H} C_8H_{14}\left\langle\begin{matrix}CH_2\\|\\CHOH\end{matrix}\right. \xrightarrow{-H_2O}$$

Camphor
(nickel oxide catalyst)

Borneol
(alumina catalyst)

$$C_8H_{14}\left\langle\begin{matrix}CH\\||\\CH\end{matrix}\right. \xrightarrow{+2H} C_8H_{14}\left\langle\begin{matrix}CH_2\\|\\CH_2\end{matrix}\right.$$

Fenchene

Camphane

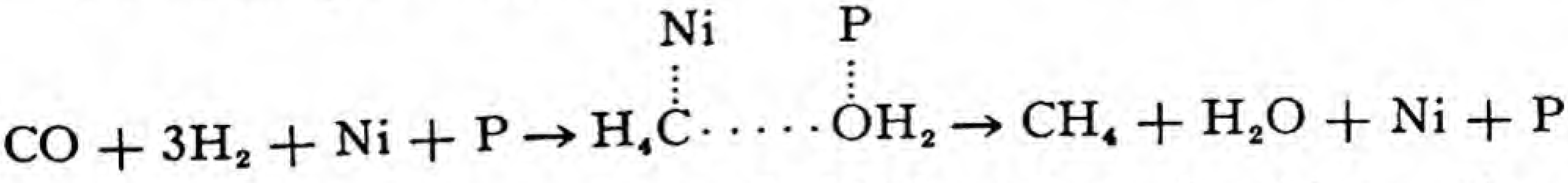
It may be seen that nickel oxide acts as a reducing catalyst, and alumina as a dehydration catalyst.

Medsforth[4] studied the promoter action of a series of dehydrating oxides in the hydrogenation of carbon monoxide to methane over nickel and explained this mechanism on the basis of intermediary formation of methyl alcohol, which, in turn, is dehydrated:

1. Hydrogenation: $CO + 2H_2 + Ni \rightarrow CH_3OH + Ni$
2. Dehydration: $CH_3OH + \text{Promoter} \rightarrow {=}CH_2 + H_2O + \text{Promoter}$
3. Hydrogenation: ${=}CH_2 + H_2 \rightarrow CH_4$

Over-all reaction: $CO + 3H_2 \rightarrow CH_4 + H_2O$

If P is the promoter, the over-all reaction may also be written:



$$CO + 3H_2 + Ni + P \rightarrow H_4\overset{\overset{Ni}{\vdots}}{C}\cdots\cdots\overset{\overset{P}{\vdots}}{O}H_2 \rightarrow CH_4 + H_2O + Ni + P$$

Medsforth's data on promoted nickel catalysts, for this reaction, are as follows:

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[4] Medsforth: *J. Chem. Soc.*, **123**, 1452 (1923).

Promoter	Optimum concentration as per cent of nickel	Maximum speed in cc/min	Temperature, °C	Method of preparation
Cerium oxide	4	620	270	Ignition of nitrate
Thorium oxide	10–12	600	270	" " "
Glucinum oxide	20	580	275	" " "
Chromium oxide	15	550	295	" " "
Aluminum oxide	15	500	297	" " "
Silica	7	430	295	Precipitated
Zirconia	18	310	280	"
Molybdenum oxide	12	220	292	Nickel nitrate Ammonium molybdate
Vanadium oxide	7	140	298	Nickel nitrate Ammonium vanadate

Promoter action has been very well illustrated graphically by Mittasch,[1] whose work, on promotion of ammonia catalysts, is classic:

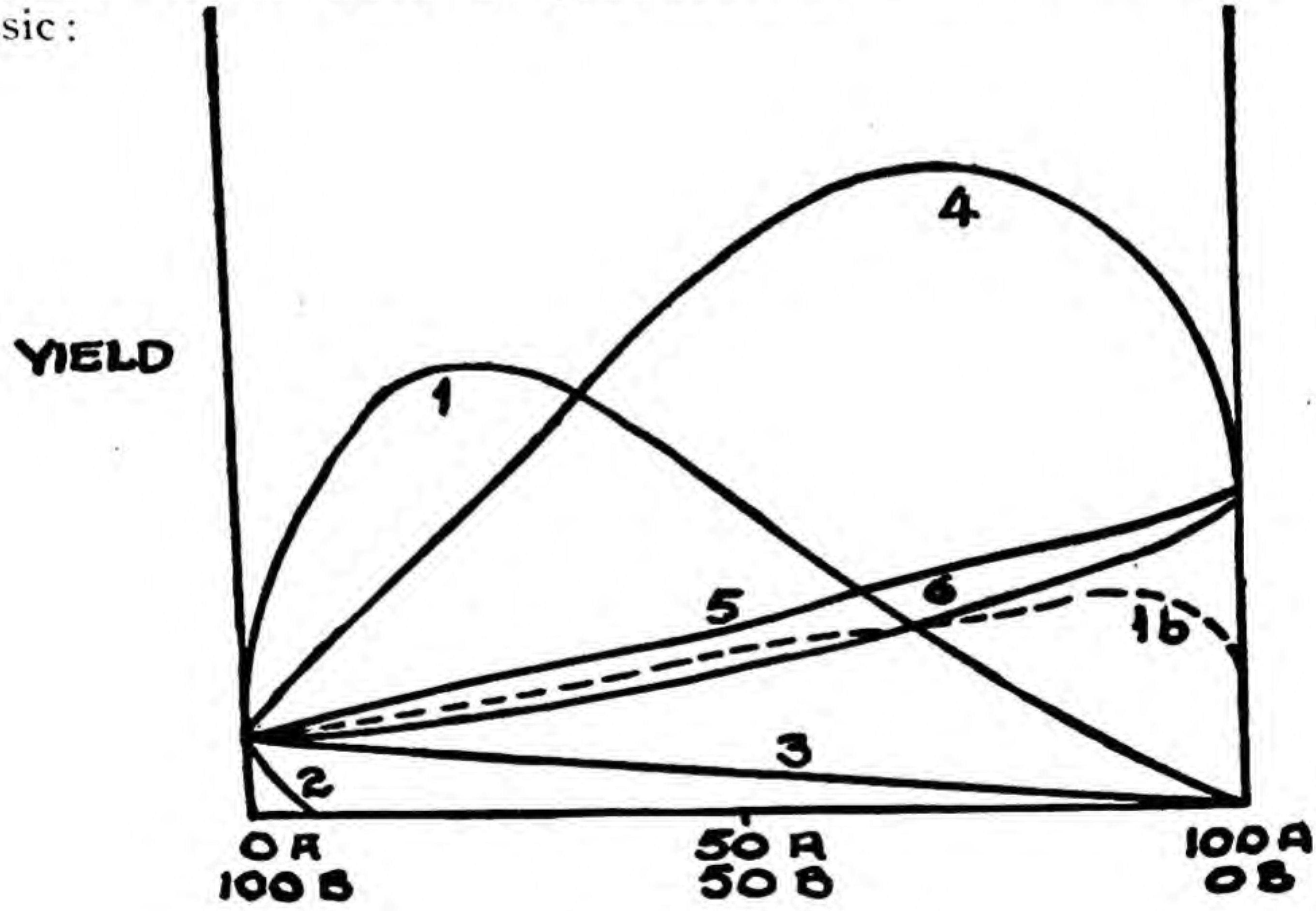

FIGURE 5

MIXED SUBSTANCES AS CATALYSTS (Mittasch)

1. Simple activation
1b. Support action
2. Simple poison action
3. Additive action (negative)
4. Mutual activation
5. Additive action (positive)
6. Mutual weakening

According to Taylor,[5] thoria, as a promoter for nickel catalysts, in the hydrogenation of CO, acts as follows: (1) supports existing active centers; (2) creates additional active surface; or (3) alters the proportions in which the reactants and reaction products are adsorbed. This is explained by assuming that during the preparation of the promoted catalyst, the promoter hinders the growth of the individual crystals of the catalyst, and thereby provides for a catalyst of smaller particle size and correspondingly larger surface.[6] Iron catalysts, containing alumina and potassium oxide as promoters, do not sinter so readily, but if an excess of promoter is used, the activity is diminished because the promoter covers the surface.[7]

The recent studies on promoters are in harmony with the findings by Baxter[8] that more gas is adsorbed by impure metals than by those of higher purity (atomic weight purity), due to the fact that the latter sinter more readily. All these observations have exceptional theoretical and technical significance for the understanding of chemical action, catalytic action in particular, because we draw our conclusions from experiments with substances containing impurities. Even reagent chemicals contain traces of other compounds and commercial grades have much larger amounts of impurities. If we could measure minute quantities, we would probably find many of the known elements in almost any inorganic chemical, and particularly in minerals occurring in nature.[9]

In part at least, the action of a promoter may be due to the formation of more or less definite compounds with the catalyst. Some promoters may also act as protectors against poisons. In the biological field, a coenzyme may act as a poison for one enzyme and as a promoter for another. Hydrogen sulfide and hydrocyanic acid are powerful poisons for catalases, but are promoters for proteases.

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[5] Taylor: *J. Phys. Chem.*, **29**, 1325 (1925).

[6] Schwab, G. M., H. S. Taylor, and R. Spence: *Catalysis from the Standpoint of Chemical Kinetics*, New York, D. Van Nostrand Co., Inc., 1937.

[7] Wyckoff and Crittenden: *J. Am. Chem. Soc.*, **47**, 2866 (1925).

[8] Baxter: *Am. Chem. J.*, **22**, 351 (1899).

[9] Lohse: *Can. Mining J.*, Dec., 1935.

GENERAL REFERENCE

Berkman, S., J. C. Morell, and Gustav Egloff: *Catalysis,* Chapter 6, Promoters and Poisons in Catalysis, New York, Reinhold Publishing Corp., 1940, p. 344. Robertson: *J. Am. Chem. Soc.,* **45**, 2512 (1923); **47**, 1299 (1925); **48**, 2072 (1926).

12. Inhibitors

Inhibition and negative catalysis are phenomena not always readily distinguishable, but we will here consider negative catalysts as retarders, and inhibitors as substances which tend to or cause complete cessation of chemical reactions. Inhibition has been extensively discussed by Bailey[1] whose elaborate reference work is highly authoritative. We can here name some typical examples only.

Inhibitors of technical interest are the anti-oxidants used in rubber manufacture (phenol, pyrocatechol, aldol-naphthyl-amine, phenyl-α-naphthylamine, etc.), and gum inhibitors[2, 3] used in gasoline. The oxidation processes, in living tissues, are inhibited by HCN. Moisture inhibits oxidation of unsaturated organic compounds, in the presence of metal catalysts.

Moureu and Dufraisse[4] have studied inhibition phenomena extensively, and found that phenols exhibit inhibitory power in a number of autoxidation processes, and that the inhibitory power increases with the increase of the number of hydroxyl groups present in the ring structure. The inhibitory power of the polyphenols is usually connected with their tendency to be oxidized to quinones, hydroquinones being a typical case (E.E.R.).

Due to their extensive use, inhibitors in cracked gasoline deserve special mention. Egloff et al.[2] investigated the relation of structure to inhibiting effectiveness of a large number of substances in their action on cracked gasoline. An accelerated oxidation test was used.

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[1] Bailey, K. C.: *The Retardation of Chemical Reactions,* London, Edward Arnold and Co., 1937.

[2] Egloff, Morrell, Lowry and Dryer: *Ind. Eng. Chem.,* **24**, 1375 (1932).

[3] Rogers and Vorhees: *Ibid.,* **25**, 520 (1933).

[4] Moureu and Dufraisse: *Compt. rend.,* **174**, 258 (1922); *ibid.,* **175**, 129 (1922); *ibid.,* **176**, 624, 797 (1923); *ibid.,* **183**, 685 (1926); *ibid.,* **184**, 1121 (1927); *ibid.,* **185**, 1545 (1927); *ibid.,* **185** II, 1545 (1927); *ibid.,* **186**, 1673 (1928); *ibid.,* **187** I, 157 (1928).

It was found that substances of pronounced inhibiting properties were those which contained phenolic and aromatic amine groups. A single hydroxyl or amine group conferred but slight inhibitory action. Most of the effective compounds contained the following groups:

(1) More than one hydroxyl or amine group
(2) An aromatic hydroxyl and amine group
(3) A single aromatic hydroxyl or amine group with one or more alkyl or amine groups.

Modifying groups in amines and phenols were most effective in the ortho or para position, but exerted some beneficial influence also when placed in meta position to the inhibiting group.

Nitro compounds, halogen compounds, and ethers were effective when they contained an aromatic amine or hydroxyl group.

The following table gives data from a six months' storage test of gasoline, containing 0.01 per cent of various inhibitors:

	Gum test; mg per 100 cc				Octane No.		Induction period, minutes
	Copper dish		Air jet				
Inhibitor	Initial	Storage	Initial	Storage	Initial	Storage	
Untreated gasoline	85	842	4	538	77	65	15
Catechol	14	7	2	12	77	75	over 240
1,5-Dihydroxynaphthalene	9	10	6	12	77	75	over 240
Pyrogallol	4	7	0	8	77	75	over 240
p-Aminophenol	6	109	0	6	77	75	over 240
Hydroquinone	2	5	0	6	77	75	55
2-Amino-5-hydroxytoluene	4	8	2	4	77	75	over 240
p-p'-Diaminodiphenylamine	6	15	6	12	77	75	over 240

Rogers and Vorhees [3] also carried out an elaborate investigation on gum inhibitors, their conclusion being that readily oxidizable compounds are the most effective inhibitors and p-aminophenols are particularly efficient.

Most of the known inhibitors are organic compounds, then come the chemical elements, chlorides, sulfates, and hydroxides, their action substantially following the order given. The inhibitors and the catalysts they inhibit are, in general, not isomorphous.[5]

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[5] Berkman, Morrell, and Egloff: *Catalysis, Inorganic and Organic,* New York, Reinhold Publishing Corp., 1940, p. 338.

13. Catalyst poisons

A great number of substances, in minute quantities, possess the property of partly or wholly destroying the activity of a catalyst. As a general rule, the more active a contact catalyst, the more readily it is poisoned.

From an extensive study of the literature, Berkman, Morrell and Egloff[1] conclude that, whereas the boiling and melting points of promoters, on the average, are high, they are low for catalytic poisons. These authors list the following groups of the common catalyst poisons:

Solid poisons	Liquid poisons	Gaseous poisons
Pb	Hg	CO
Cu	H_2O	CO_2
Cyanide	Ethyl alcohol	H_2S
Arsenates	Amyl alcohol	S
Unsaponifiable matter		Cl_2
		O_2
		H_2O

Senter[2] made an interesting comparison of the poisoning effect of a series of substances on colloidal platinum (data obtained with different preparations) and haemase (enzyme in the red blood corpuscles) in the decomposition of hydrogen peroxide:

Poison	Colloidal platinum (Bredig)	Haemase (Senter)
H_2S	M/300,000	M/1,000,000
HCN	M/20,000,000	M/1,000,000
$HgCl_2$	M/2,000,000	M/2,000,000
$HgBr_2$	—	M/300,000
$Hg(CN)_2$	M/200,000	M/300,000
I_2 in KI	M/5,000,000	M/50,000
$NH_2OH \cdot HCl$	M/25,000	M/80,000
$C_6H_5NH \cdot NH_2$	—	M/20,000
$C_6H_5NH_2$	M/5,000	M/400
As_2O_3	M/50	No poisoning at M/2,000
CO	Very poisonous	No poisoning
HCl	M/3,000	M/100,000

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[1] Berkman, S., J. C. Morrell, and G. Egloff: *Catalysis, Inorganic and Organic*, New York, Reinhold Publishing Corp., 1940, p. 344.

[2] Senter: *Z. physik. Chem.*, 51, 701 (1905).

Poison	Colloidal platinum (Baedig)	Haemase (Senter)
N_4HCl	M/200	M/1,000
HNO_3	No poisoning	M/250,000
H_2SO_4	No poisoning	M/50,000
KNO_3	No poisoning	M/40,000
$KClO_3$	Slight poisoning	M/40,000

Bancroft[3] concludes that the poisons are strongly adsorbed by the catalytic agent and, therefore, prevent or decrease the adsorption of H_2O_2. As discussed under chemical reactions on surfaces (page 31), promoters cover a considerable part of the surface of a catalyst, and in view of this, Bancroft's conclusion is reasonable.

Kelber[4] studied the action of several catalyst poisons on nickel catalysts prepared by various methods for hydrogenation:

(1) Catalyst prepared from basic nickel carbonate reduced at 450°C in a current of hydrogen.
(2) Catalyst prepared as (1), but reduced at 310°C.
(3) Basic nickel carbonate on a carrier of Florida Bleaching Earth (Owl Commercial Company) reduced in a current of hydrogen at 450°C.

The poisons, the effect of which was tried out, were: KCN, HCN, H_2S, and CS_2. Catalyst (1) was most susceptible to poisoning, and catalyst (3), which was supported, was least susceptible. Kelber measured the hydrogen, taken up by cinnamic acid during different periods of time, in the absence and presence of a poison, the data with KCN as a poisoning agent being as follows: (cc hydrogen at O°C and 760 mm)

Time in minutes:	5	10	15	20	25	30	35	40	50	60
Catalyst (1):										
No poison	7.2	13.9	21.3	30.7	39.4	44.9	54.4	65.2	75.3	85
0.00005 gram KCN	2.7	6.3	9.4	12.1	15.3	19.7	23.7	26.4	33.1	41.2
Catalyst (2):										
No poison	54.2	103.3	115.5							
0.001 gram KCN	3.5	7	13	17	26.9	30.3	35.4	38.9	46.1	54.8
Catalyst (3):										
No poison	43	80.6	110	116.1						
0.002 gram KCN	8.1	17	24.2	32.3	39.4	50.2	57.3	66.3	83.3	99.4

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[3] Bancroft: *J. Phys. Chem.*, **21**, 734 (1917).

[4] Kelber: *Ber.*, **49**, 1868 (1916).

Kelber's data are extensive and for details, the original paper should be consulted. Catalyst poisons, for nickel hydrogenation catalysts, have been studied extensively, and will be discussed elsewhere.

Ipatieff [5] studied the influence of some catalyst poisons on a hydrogenation catalyst (copper activated with nickel) for hydrogenation of benzene, the amounts required for complete deactivation being:

	Weight per cent	Mol per cent
Lead *	0.09	0.03
Bismuth	0.16	0.05
Cadmium	0.20	0.12
Sodium chloride	0.15	0.16
Sodium sulfate	0.38	0.17

---

* In concentrations of 0.01%, or smaller, lead functions as a promoter.

The influence of poisons on platinum metals has been studied by Maxted.[6] In one paper [*J. Chem. Soc.*, **115**, 1050 (1919)], Maxted shows the influence of H_2S on the occlusion of hydrogen by palladium:

		Occlusive power for hydrogen	
Weight of palladium, grams	Weight of sulfur, grams	absorbed, cc at N.T.P.	Vol. subseq. evolved, cc at N.T.P.
0.6	0.0117	31.7	31.6
0.6	0.0117	31.8	32.4
0.6	0.0117	31.3	31.0
0.6	0.0117	30.7	...
0.6	0.0242	21.2	21.6
0.54	0.0328	8.4	8.2
0.54	0.0328	8.0	7.9
0.54	0.0328	7.7	7.9

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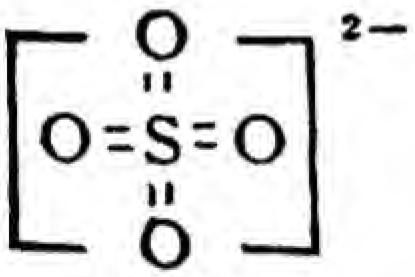
[5] Ipatieff: *J. Phys. Chem.*, **45**, 431 (1941).

[6] Maxted, and Maxted et al.: *J. Chem. Soc.*, **115**, 1050 (1919); *ibid.*, **117**, 1501, (1920); *ibid.*, **119**, 225 (1921); *ibid.*, **122**, 1760 (1922); *ibid.*, **127**, 73, (1925); *ibid.*, with Lewis, 502 (1933); *ibid.*, with Stone, 26 (1934); *ibid.*, 672 (1934); *ibid.*, with Evans, 455 (1938); *ibid.*, 2071 (1938); *ibid.*, with Marsden, 839 (1938); *ibid.*, with Moon, 1228 (1938); *ibid.*, **252**, 469 (1940); *J. Soc. Chem. Ind. (Trans.)* **53**, 102 (1934).

The sulfur uptake corresponds to the formation of Pd_4S, although no specific evidence for the formation of this sulfide was revealed.

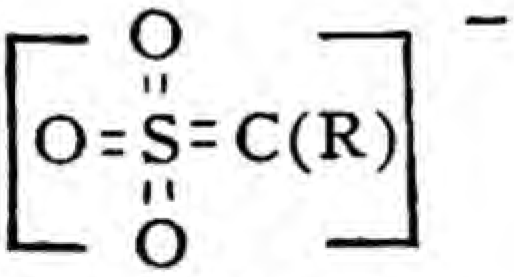
In studies on catalytic toxicity and chemical structure, Maxted [*J. Chem. Soc.*, 252, 469 (1940)] came to the conclusion that the ability of sulfur, tellurium, and selenium to act as catalyst poisons is lost if they are associated with a completely shared electron octet. An exception to this occurs when hydrogen is a part of the ion because hydrogen is unable to shield the toxic elements from acting as poisons.

The experiments were carried out with platinum black, in the hydrogenation of crotonic acid or ethyl crotonate, at 25°C. The explanatory configurations and the relative toxicities are as follows:



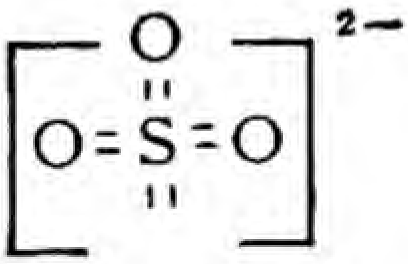
$\left[O{=}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{=}O\right]^{2-}$

I
non-toxic
sulfate ion



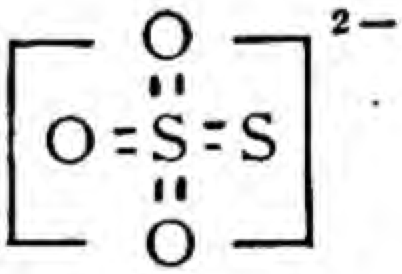
$\left[O{=}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{=}C(R)\right]^{-}$

II
non-toxic
sulfonate ion



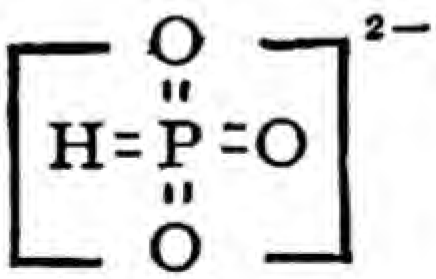
$\left[O{=}\underset{\cdot\cdot}{\overset{\overset{O}{\|}}{S}}{=}O\right]^{2-}$

III
strongly toxic
sulfite ion
(also selenite and
tellurite ions)



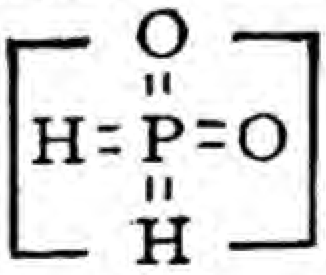
$\left[O{=}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{=}S\right]^{2-}$

IV
strongly toxic
thiosulfate ion



$\left[H{=}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{P}}{=}O\right]^{2-}$

toxic
phosphite ion



$\left[H{=}\underset{\underset{H}{\|}}{\overset{\overset{O}{\|}}{P}}{=}O\right]$

toxic
hypophosphite ion

Ion	Relative toxicity
Phosphite	1
Thiosulfate	1.05
Selenite	1.26
Tellurite	1.37
Sulfite	1.42
Tetrathionate	2.26
Sulfide	2.26
Hypophosphite	2.75

The poisoning of nickel and and platinum catalysts by chlorine has been studied by Boswell and Bayley[6a] who concluded that the chlorine destroyed the surface film of water, which, they assume, is the seat of catalytic action.

An exceptionally clear analysis of a complicated poisoning effect of a catalyst has been presented by Emmett and Brunauer[7] who studied the poisoning effect of water vapor in ammonia synthesis over iron contacts, at 450°C, and up to 100 atmospheres pressure. The water vapor ranged from 0.08 to 0.64 per cent. The conclusion was that the amount of oxygen, retained by the catalyst, was proportional to $\sqrt{P_{H_2O}/P_{H_2}}$, and that very active catalysts are capable of retaining more oxygen than the less active ones. This poisoning effect is reversible, with a slight permanent injury to the catalyst.

Beech, Smith and Wheeler[8] studied the poisoning of nickel surfaces with carbon monoxide and oxygen and found that such poisoned surfaces will still adsorb 20% of the amount of hydrogen that a clean surface would have taken up. The activity of the catalyst surface is inversely proportional to the degree of poisoning. This work is exceedingly important in its bearing upon hydrogenation reactions.

Balandin[9] has developed the following equation for the reaction velocity in case of poisoning of the catalyst:

$$\frac{dC}{dt} = k\frac{\alpha(C_o - C)}{1 + \alpha(C_o - C) + \beta C_1}$$

Where C_o is the initial concentration of the reactant, C is the amount of C_o which is converted at time t, C_1 is the concentration of poison, α and β are coefficients which are proportional to the life of the molecules on the surface of the catalyst, and k is the velocity constant, depending on the surface area.

Whereas catalyst poisons are mostly discussed from the point of view of their adverse effect on positive catalysis, it should be borne in mind that catalyst poisons may be used to repress undesirable reactions. It also requires mention that catalysts may lose activity due to sintering caused by exposure of the catalyst to too high temperature for a shorter or longer time, as the case may be. This effect is brought about by a collapse of the surface structure of the catalyst.

[6a] Boswell and Bayley: *J. Phys. Chem.*, **29**; 11, 679 (1925).

[7] Emmett and Brunauer: *J. Am. Chem. Soc.*, **52**, 2682 (1930).

[8] Beech, Smith and Wheeler: *Proc. Roy. Soc. (London)*, **A 177**, 62 (1940).

[9] Balandin: *Z. physik. Chem.*, **B2**, 289, (1929).

14. Homogeneous catalytic reactions

A catalytic reaction is said to be homogeneous when the reactants and the catalyst are physically of the same state and phase. Practically, homogeneous catalytic reactions take place only in gases or liquids, as homogeneous reactions in solids are doubtful.

In studying homogeneous catalytic reactions, it should be borne in mind that all of our experiments are carried out in vessels of limited content, having walls which exert more or less catalytic effects, although these effects are very frequently overlooked and unaccounted for. It is difficult, in a given case, to be sure as to how much of the observed effects are actually due to homogeneous catalysis.

In the following, a variety of examples of homogeneous catalytic reactions is presented in order to demonstrate some of the reaction mechanisms involved.

In nature, however, where volumes are much greater relative to surfaces, as in the atmosphere or in oceans and lakes, homogeneous catalysis must play a greater part. In this connection, it is interesting to recall a recent report about the identification, in interstellar space, of carbon hydride, CH, a highly unsaturated compound. The atmosphere is so rare there that about one atom or molecule is found per cubic yard.[1]

When a substance decomposes under the influence of a catalyst, the reaction may actually be bimolecular, yet, it follows the monomolecular equation, since the concentration of the catalyst is constant. Homogeneous gas reactions are most frequently bimolecular and in such reactions, combination or decomposition may occur when there is an impact between two molecules.

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[1] Mott-Smith: *Science*, **96** (1942) (Science Supplement).

The rate of change in an ordinary bimolecular reaction, $A + B = C + D$, is determined by

$$1.\quad \frac{dx}{dt} = k(a - x)(b - x)$$

$$2.\quad k = \frac{1}{t(a - b)} \ln \frac{b(a - x)}{a(b - x)}$$

If in this reaction, A is a catalyst, the rate of change is:[2]

$$3.\quad \frac{dx}{dt} = k \cdot a(b - x)$$

$$4.\quad k = \frac{1}{at} \ln \frac{b}{b - x}$$

The reason for this is that the concentration of the catalyst, a, is not supposed to decrease during the course of the reaction, and if it did, it would be by a side reaction.

If, in the reaction $A + B + C = E + F + G$, A is a catalyst, then:

$$5.\quad \frac{dx}{dt} = k \cdot a(b - x)(c - x)$$

$$6.\quad k = \frac{1}{at}(b - c)(c - a) \ln \frac{c(b - x)}{b(c - x)}$$

If the velocity equation is of the first, second, or third order, the reaction is probably homogeneous although chain reactions are not excluded. However, if the reaction is of zero order, a fraction of a number, or a number above three, it is most likely that the reaction is heterogenous or a chain reaction.[3]

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[2] Rice, F. O.: *The Mechanism of Homogeneous Organic Reactions from the Physical-Chemical Standpoint,* New York, Reinhold Publishing Corp., 1928, p. 36.

[3] Schumacher, H. J.: *Chemische Gasreaktionen,* Dresden, Theodor Steinkopff, 1938.

Christiansen[4] assumes that the velocity of an elementary reaction is given by the concentration of the reactants and their distribution, his reasoning being that the chemical reactions, we actually observe, are the resultants of several components which are to be considered as elementary reactions that cannot be further resolved.

The velocity of an elementary reaction is completely determined by the concentration of the reacting molecules and by a temperature function, $r_{1,2}e^{-\frac{Q_{1,2}}{RT}}$. Certain bimolecular reactions proceed with a velocity given by

$$1. \quad v_{1,2} = C_1 \cdot C_2 \cdot r_{1,2}e^{-\frac{Q_{1,2}}{RT}}$$

$\nu_{1,2}$ being a factor of approximately the same value as $s_{1,2}$ in the equation for the number of collisions $(c_{1,2})$ between the same molecules:

$$2. \quad c_{1,2} = c_1 \cdot c_2 \cdot s_{1,2}$$

As shown by Herzfeld

$$3. \quad \nu_{1,2} = s_{1,2}$$

assuming that the condition for reaction is that the two molecules collide with a relative velocity which, in the moment of collision, exceeds a certain limit.

The temperature function, $r_{1,2}\,e^{-\frac{Q_{1,2}}{RT}}$, expresses the frequency with which certain characteristic combinations of molecules 1 and 2 occur in the gas, at unit concentrations, i.e., the distribution of the molecules or pairs of molecules in the different possible states.

Whether a chemical reaction is catalytic or non-catalytic, it is obvious that in order to react, the reactants must come close to each other and in a proper spatial position. In non-catalytic double decomposition:

$$Na_2SO_4 + BaCl_2 \rightarrow \underset{\text{insoluble}}{BaSO_4} + 2NaCl$$

the following ions participate:

$$2Na^+ + SO_4^{--} + Ba^{++} + 2Cl^- = \underset{\text{insoluble}}{BaSO_4} + 2Na^+ + 2Cl^-$$

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[4] Christiansen: *Trans. Faraday Soc.*, **24**, 596 (1928); Herzfeld: *Ann. Physik*, **59**, 635 (1919).

In order to combine Ba^{++} and SO_4^{--}, these two ions must be in juxtaposition and collide within a certain reaction sphere and in the proper mutual spatial position, for instance, according to the following arbitrary, two-dimensional reaction configuration:

$$\left(\begin{array}{ccc} \mathrm{Na^+} & \mathrm{SO_4^{--}} & \mathrm{Na^+} \\ \mathrm{Cl^-} & \mathrm{Ba^{++}} & \mathrm{Cl^-} \\ \multicolumn{3}{c}{\scriptstyle\text{spatial reaction sphere}} \end{array}\right) \longrightarrow \left(\begin{array}{cc} \mathrm{Na^+} & \mathrm{Cl^-} \\ \mathrm{Cl^-} & \mathrm{Na^+} \end{array}\right) + \underset{\text{precipitate}}{\mathrm{BaSO_4}}$$

It is obvious that such reaction spheres must be formed throughout the solution, and that the velocity of formation of this reaction sphere is the determining factor in the velocity of the reaction and, consequently, is an intermediate step, necessary for the combining action. For the case at hand, it is a well known fact that the speed of precipitation of $BaSO_4$ in the cold, from very dilute solutions with respect to SO_4^{--}, is much smaller than in hot solutions where the kinetic energy of the reactants is higher (Lohse).

Homogeneous gas reactions have been thoroughly investigated by Hinshelwood[5] who made the conclusion that the formation of intermediate compounds is rare in homogeneous gas catalysis, the rate of which is determined by the rate of collisions and activations.

However, in solutions, conditions are different because the reacting substances form associations or compounds with the solvent and in many known cases, actual intermediate compounds are formed in reactions occurring in successive stages. The formation of such molecular addition compounds, in solutions, has been extensively studied by Kendal et al[6, 7, 8, 9] and Rice.[2]

Euler et al[10] conclude that acids and bases form compounds of the type of salts with their substrates when catalyzing hydrolytic reactions, and the catalyst is added to "just that group of the substrate in which the hydrolysis takes place."

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[5] Hinshelwood: *Trans. Faraday Soc.*, **24**, 552 (1928).

[6] Kendall: *J. Am. Chem. Soc.*, **43**, 1416 (1921); *ibid.*, **44**, 717 (1922).

[7] Kendall and Booge: *Ibid.*, **38**, 1712 (1916).

[8] Kendall, Booge, and Andrews: *Ibid.*, **39**, 2303 (1917).

[9] Kendall and Harrison: *Trans. Faraday Soc.*, **24**, 588 (1928).

[10] Euler: *Trans. Faraday Soc.*, **24**, 651 (1928).

a. Homogeneous catalytic chain reactions

Oxidation of carbon monoxide is not dependent on the presence of moisture, but the reaction mechanisms seem to be different for the dry and the wet oxidation.

Dry Combustion of CO

(a) (Hinshelwood):[11] The dry gases explode between two limiting pressures, the lower limit of which appears to be controlled by the breaking of the chains at the wall of the reaction vessel. The upper limit appears to be determined by gas deactivation.

Assuming that the chains originate from centers on the wall of the vessel, the following reactions are possible on the basis of branching chains:

1. $CO + O_2 = CO_2 + O$	primary wall reaction
2. $O + CO + O_2 = CO_2 + 2O$	branched chains
3. $O + CO + CO = CO_2 + CO$	interruption of the chain in the gas
4. $O + O + \text{inert gas} = O_2$	
5. $O + CO + \text{inert gas} = CO_2$	
6. $O + CO = CO_2$	breaks the chain at the wall, determines the lower limit

Wet Combustion of CO

(b) (Frankenburger):[12] As the most possible reaction mechaism is considered the one in which the water molecule acts as an oxygen carrier:

1. $CO + H_2O = CO_2 + H_2$

2. $H_2 + \frac{1}{2}O_2 = H_2O$, etc.

The second elementary process, in this mechanism, is nothing but the combustion of hydrogen which proceeds by a chain reaction, with intermediary formation of very reactive hydrogen atoms and hydroxyl radicals which take part in the combustion process of carbon monoxide:

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[11] Hinshelwood: *Trans. Faraday Soc.*, 27, 176 (1931).

[12] Frankenburger, W.: *Katalytische Umsetzungen in homogenen und enzymatischen Systemen*, Leipzig, Akademische Verlagsgesellschaft, 1937.

1. $H + O_2 + CO \rightarrow CO_2 + OH$
2. $OH + CO \rightarrow CO_2 + H$
3. $H + O_2 + CO \rightarrow CO_2 + OH$, etc.

Oxidation of Hydrogen

(Hinshelwood et al):[13, 14] This reaction is considered heterogeneous below 500°C, being accelerated by wall catalysis; but above 520°C, the wall reaction retards the formation of water, whereas it is accelerated by steam, argon, nitrogen, and helium, indicating that the collisions are largely elastic. At high pressures, the following reactions probably occur:

1. $2H_2 + O_2 \rightarrow \underset{\text{(carry large excess of energy)}}{\underline{2H_2O}}$
2. $\underline{H_2O} + O_2 \rightarrow H_2O + \underline{O_2}$
3. $2H_2 + \underline{O_2} \rightarrow \underline{2H_2O}$

At low pressures, a different process takes place:

1. $H_2 + O_2 \rightarrow H_2O_2$
2. $H_2O_2 + H_2 \rightarrow \underset{\text{(carry large excess of energy)}}{\underline{2H_2O}}$
3. $\underline{H_2O} + O_2 \rightarrow H_2O + \underline{O_2}$
4. $\underline{O_2} + H_2 \rightarrow H_2O_2$

Chain Reactions Induced by Alkali Vapor

Polányi[15] found that a sodium or potassium atom, when brought into a mixture of chlorine and hydrogen, induces the

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[13] Gibson and Hinshelwood: *Proc. Roy. Soc. (London),* **A 119,** 591 (1928).

[14] Hinshelwood: *Trans. Faraday Soc.,* **24,** 552 (1928).

[15] Polányi: *Ibid.,* **24,** 606 (1928).

formation of hydrochloric acid, several thousand molecules of HCl resulting from each alkali metal atom.

The reaction mechanism is as follows:

1. $Na + Cl_2 \rightarrow NaCl + Cl$

which is followed by a Nernst reaction chain:

2. $Cl + H_2 \rightarrow HCl + H$
3. $H + Cl_2 \rightarrow HCl + Cl$, etc.

The inducing action of alkali metal vapors, in a mixture of Cl_2 with a hydrocarbon, is as follows:

1. $Na + Cl_2 \rightarrow NaCl + Cl$
2. $Cl + CH_4 \rightarrow HCl + CH_3$
3. $CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$

The length of these chains is limited, because the free atoms or radicals react with impurities or unite at the walls of the reaction vessel, to form saturated molecules.

The effect of the wall reaction is shown in the following phenomena:

(1) The chain length (i.e., the number of reactions in a chain) is shortened by reducing the partial pressure of the hydrogen.
(2) Admixture of nitrogen increases the chain length.
(3) The chain length is ten times as great, if the wall is covered with a compact layer of sodium chloride.

The chain length is also shortened by bromine, iodine, $HgCl_2$ and $HgBr_2$. The bromine inhibition is due to the fact that Br_2 reacts with the free H atoms (1) or the free CH_3 radicals (2):

1. $H + Br_2 \rightarrow HBr + Br$
2. $CH_3 + Br_2 \rightarrow CH_3Br + Br$

It was also found that the divalent metals, Cd, Zn, and Mg, and the metalloids, As and P, had abundant inducing effect of the same type as the alkali metals. Zn and Cd were studied most, and the reactions were as follows:

1. $Cd + Cl_2 \rightarrow CdCl + Cl$
2. $Zn + Cl_2 \rightarrow ZnCl + Cl$

It was concluded that between Zn and Cl_2 at least 5×10^3 collisions can take place, without formation of the dichloride and, in the case of Cd, this limit is approximately 10^5 collisions. These reactions also were inhibited by bromine.

Decomposition of Ethane

This reaction is interpreted to take place as follows: [16]

1. $C_2H_6 \rightarrow 2CH_3$ (endothermal)
2. $CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$
3. $$\left.\begin{array}{l} C_2H_5 \rightarrow C_2H_4 + H \\ H + C_2H_6 \rightarrow H_2 + C_2H_5 \end{array}\right\} \text{chain reaction}$$
4. $H + C_2H_5 \rightarrow C_2H_6$

It is assumed that this type of reaction mechanism is quite general in decomposition reactions (e.g., in the cracking of hydrocarbons, and in internal combustion engines).

Explosion Limits [17, 18]

A reaction may proceed with very low or non-measurable velocity, but at pressures above or below a certain critical value, the reaction velocity may suddenly become extremely high or explosive. An example is the reaction between phosphorus vapor and oxygen. The lower critical explosion limit may be explained, according to Semenoff,[18] by a chain mechanism, the chains being broken at the wall of the vessel. However, the wall effect decreases rapidly with increasing pressure and at a certain pressure, the number of activated molecules, starting chains, exceeds the number of chains broken at the wall and at that point, the reaction velocity increases very rapidly, and especially so, if the thermal conductivity is small. Dilution with an inert gas lowers the critical reaction pressure, because it delays the active molecules or prevents them from reaching the wall.

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[16] Rice and Herzfeld: *J. Am. Chem. Soc.*, **56**, 284 (1934).
[17] Chariton and Walta: *Z. Physik*, **39**, 547 (1926).
[18] Semenoff: *Z. Physik*, **46**, 109 (1926).

The upper critical explosion limit may be explained by the fact that, at higher pressures, the effect of deactivation, by non-elastic collisions in the gas phase, increases and by the combined decrease of deactivation at the walls and in the gas phase, the reaction may suddenly proceed with considerable velocity and explosion may occur, and the reaction velocity suddenly fall to a very low value or nil.

b. Homogeneous vapor and gas reactions

Decomposition of acetaldehyde:[18a]

$$CH_3CHO \rightarrow CH_4 + CO$$

occurs at 500°C or above. At 400°C, the rate of reaction is very low, except in the presence of small quantities of iodine. The reaction is unimolecular with respect to the aldehyde, consequently:

$$-d[CH_3CHO]/dt = k[CH_3CHO][I_2]$$

$[I_2]$ being constant, we have:

$$k = \frac{1}{t} \log \frac{a}{a - x}$$

where a and x, respectively, are the initial amount of aldehyde and the amount decomposed after t seconds. In the following example, the initial pressure of the aldehyde was 239 mm.

[18a] Hinshelwood, Clusius, and Hadman: *Proc. Roy. Soc. (London)*, **A 128**, 88 (1930).

Decomposition of acetaldehyde

Seconds	x	k_{10} (decimal logarithms)
7	20	0.0061
15	40	0.0060
32	75	0.0059
42	90	0.0057
56	110	0.0056
81	140	0.0057
102	160	0.0059
132	180	0.0061
∞	213	—
	Average:	0.00588

The influence of catalyst concentration

Catalyst, mm	k_{10}	k_{10}/catalyst $\times 10^4$
10	0.00193	1.93
20	0.00377	1.89
30	0.00559	1.86

Decomposition of Ethers

In the vapor phase, in the presence of iodine, this reaction proceeds according to the following mechanism:[19]

(1) Methylethylether decomposed catalytically between 460 and 550°C:

1. $CH_3{\cdot}O{\cdot}C_2H_5 \rightarrow CH_4 + CH_3{\cdot}CHO$
2. $CH_3{\cdot}CHO \rightarrow CH_4 + CO$

(2) Methylisopropylether decomposes catalytically between 450 and 520°C:

1. $CH_3{\cdot}O{\cdot}CH(CH_3)_2 \rightarrow CH_4 + CO(CH_3)_2$
2. $CH_3{\cdot}O{\cdot}CH(CH_3)_2 \rightarrow CH_2O + C_3H_8 \rightarrow CO + H_2 + C_3H_8$

The catalyst attacks the molecule at a specific point and the reaction can, in every case, be interpreted as the migration of a hydrogen atom from a carbon atom, which is also connected by an oxygen atom to a second carbon atom.

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[19] Clusius: *J. Chem. Soc.*, 2607 (1930).

The heats of activation of some ethers, decomposed by iodine catalysis, are lower for the catalyzed than for the non-catalyzed process:[20]

Substance decomposed	Heat of activation in calories Non-catalyzed	 Catalyzed
Dimethylether	65,000	—
Methylethylether	47,000	38,000
Diethylether	53,000	34,000
Diisopropylether	60,500	28,500
Acetaldehyde	45,500	32,500

Reaction between NO and $(CN)_2$

When a mixture of nitric oxide and cyanogen, each at ½ to ⅓ atmosphere partial pressure, is radiated by ultraviolet light of 360 to 220 $\mu\mu$ (cooled mercury vapor lamp), the following reactions take place:[21]

1. $4NO \rightarrow N_2 + 2NO_2$
2. $4NO + (CN)_2 \rightarrow 3N_2 + 2CO_2$

Reaction (1) is about six times as extensive as reaction (2). Reaction (1) is catalyzed by cyanogen, but neither reaction occurs in the absence of a small trace of oxygen which forms NO_2. The NO_2 gradually accumulates during the reaction, with autocatalytic effect. Indications are that a comparatively stable intermediate compound, NOCN, is formed, with the fall of pressure in the system, when the light is cut off:

$$3.\quad 2NO + (CN)_2 \underset{\text{light}\,(2)}{\overset{\text{light}\,(1)}{\rightleftarrows}} 2NOCN$$

the reaction to the right being catalyzed or sensitized by NO_2.

The nitrosyl cyanide decays in the dark, according to:

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[20] **Clusius and Hinshelwood:** *Z. Elektrochem.*, **36**, 748 (1930).

[21] **Norrish and Smith:** *Trans. Faraday Soc.*, **24**, 620 (1928).

$$4.\quad \left.\begin{aligned} &2NOCN \rightarrow N_2 + O_2 + (CN)_2 \\ &2NO + O_2 \rightarrow 2NO_2 \rightleftarrows N_2O_4 \end{aligned}\right\}$$

By addition of reactions (3) and (4) and the usual elimination of the intermediary substances, reaction (1) results. By combining the reaction

$$5.\quad NOCN + NO_2 \xrightleftharpoons{\text{light}} NO + CO_2 + N_2$$

with reaction (3), reaction (2) results as a side reaction.

The authors state that an analogous mechanism has been observed in the system nitric oxide-cyanogen chloride.

This mechanism illustrates the working of a catalyst (cyanogen) in a homogeneous reaction, promoted by a trace of oxygen and occurring with the formation of an unstable intermediate compound (nitrosyl cyanide).

c. *Homogeneous reactions in liquid phase*

In liquid phase reactions, we have to consider ionization in aqueous solvents, associations between solute and solvent, and other solvent effects, and, as in gas reactions, wall reactions. Bimolecular reactions, in solvents, are much slower than in the gaseous state, due to the deactivating influence of the solvent molecules[22] and the effectiveness of bimolecular collisions, between molecules with appropriate energies, appears to be several powers of ten smaller in the presence of a solvent.[23] Catalysis, in solutions, is very widespread, and there is reason to believe that the majority of reactions, in liquids, are catalytically affected.

d. *Acid-base catalysis*

The activity, in acid-base catalysis, is caused by both the characteristic ions, H^+ and OH^- respectively, and the undissociated part of the acid or base molecule (see Dawson et al., *J. Chem. Soc.*, 1927–1930).

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[22] Christiansen: *Z. physik. Chem.*, **113**, 35 (1924).

[23] Hinshelwood: *Trans. Faraday Soc.*, **24**, 554 (1928).

Definition of Acids and Bases

(Brönsted, Lowry):[24, 25] According to the classical conceptions, acids and bases are substances which are capable of dissociating into hydrogen and hydroxyl ions respectively. However, this definition does not account for the behaviour of acids and bases in non-aqueous solutions, nor for their complementary but opposite properties. To overcome these difficulties, an acid is defined as a proton donor, the proton being the unhydrated hydrogen ion. Consequently, a base is defined as a substance which can unite with protons, i.e., it is a proton acceptor. This is expressed by:

$$\underset{\text{acid}}{A} \rightleftarrows \underset{\text{proton}}{H^+} + \underset{\text{base}}{B}$$

where A is an acid and B is a base. For the case of acetic acid we have:

$$\underset{\text{acid}}{CH_3COOH} \rightleftarrows H^+ + \underset{\text{base}}{CH_3COO^-}$$

As strong acids are almost completely ionized in solutions, their anions do not tend to form appreciable amounts of non-dissociated acids, and consequently, their anions are not bases.

Cations of weak bases are to be regarded as acids (cation acids):

$$NH_4^+ \rightleftarrows H^+ + NH_3$$

Anions of weak acids are likewise to be regarded as acids (anion acids):

$$HCO_3^- \rightleftarrows CO_3^{--} + H^+$$

In considering these definition schemes, it should be borne in mind that a proton cannot exist in the free state, but can only be transferred from one molecule to another.

In actual practice, an acid-base reaction can, by definition, be written as a double reaction between two pairs of the corresponding acids and bases (i.e., protolytic reaction):

$$\underset{\text{acid}_1}{A_1} + \underset{\text{base}_2}{B_2} \rightleftarrows \underset{\text{acid}_2}{A_2} + \underset{\text{base}_1}{B_1}$$

$$\underset{\text{acid}_1}{CH_3COOH} + \underset{\text{base}_2}{H_2O} \rightleftarrows \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{CH_3COO^-}$$

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[24] Brönsted, J. N.: *Physical Chemistry*, London, William Heinemann, Ltd., 1937, p. 204.

[25] Lowry: *J. Chem. Soc.*, 1923 (1927).

$$\underset{\text{base}_1}{NH_3} + \underset{\text{acid}_2}{H_2O} \rightleftarrows \underset{\text{acid}_1}{NH_4^+} + \underset{\text{base}_2}{OH^-}$$

It is also obvious that electrolytic dissociation of acids and bases only takes place in solvents, which themselves can take part in the protolytic reaction, such as water.

If a solvent molecule possesses amphoteric properties and is denoted by M, its acid-base functions are written as:

$$M \rightleftarrows M^- + H^+$$

$$M^+ \rightleftarrows M + H^+$$

For water, the corresponding equations are:

$$H_2O \rightleftarrows OH^- + H^+$$

$$H_3O^+ \rightleftarrows H_2O + H^+$$

By adding these two equations, the over-all reaction is:

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$

A detailed analysis of the kinetics of acid and base catalysis has been given by Skrabal,[26] on the assumption that acid or base catalyzed reactions proceed through the formation of unstable intermediate bodies. From a kinetic point of view, two types of intermediate bodies are postulated, viz.: (a) a type in which the intermediate body is in equilibrium with the initial materials (Arrhenius type); and (b) a type which is not controlled by this equilibrium (van't Hoff type), this type of intermediate body being less stable than the type under (a).

Furthermore, according to Skrabal's deduction, Lowry's electrolytic theory of catalysis (described above) accords best with experimental facts, the intermediate bodies postulated by this theory, being of the van't Hoff type.

e. Salt effects

The catalytic efficiency of a molecular species is, to some extent, dependent on the total ionic content of the solution, and the effect of neùtral salts, in acid-base catalysis, is very significant. The salt effect is partly due to the total ionic strength of the solution, primary salt effect, and partly due to ions in common with the catalyst or the substrate, secondary salt effect.

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[26] Skrabal: *Trans. Faraday Soc.*, **24**, 687 (1928).

Arrhenius[27] observed that the addition of neutral salts increases the acid catalysis, by weak acids, of the cane sugar inversion in proportion to their concentration and that increasing the concentration of acid causes an increase of velocity which grows more rapidly than the hydrogen ion concentration. If k is the constant for the rate of inversion and m the acid concentration, it follows that:

$$k = am + bm^2$$

Arrhenius considered this increase of activity to be due to increase in ionization, a view which has been supported later.[28]

Harned and Akerlöf[29] studied the primary salt effect in more than six reactions and found no uniformity on which to base a simple and general rule. The addition of salt, in acid catalysis, usually tends to increase the reaction velocity, whereas in hydroxide catalysis the reverse usually, but not always, is true.

The velocity of hydrolysis of ethyl acetate by 0.1 N HCl in various salt solutions is listed in the following table. The velocity constant, k, at zero salt concentration is 28.8. The values in the table are $k \times 10^5$:[30, 31]

	1 N salt	2 N salt	3 N salt
KCl	34.1	39.4	44.6
NaCl	35.7	43.1	52.3
LiCl	33.6	38.0	42.2
NaBr	33.1	37.4	41.7

Dawson[31a, 39] studied the accelerating effect of different acids in salt concentrations up to four mols per liter. For hydrochloric acid, the velocity increased proportionally to the salt concentration up to a concentration of the latter of three mols per liter. Above that concentration of neutral salt, the velocity increases more rapidly. Dichloracetic, chloracetic, and acetic acids behave quite differently. At low salt concentrations, the salt effect is greatest for the acetic acids and least for hydrochloric acid, whereas at high concentrations of the neutral salt, this order is reversed, the acetic acids showing decrease in catalytic activity.

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[27] Arrhenius: *Z. physik. Chem.*, **4**, 226 (1889).

[28] Brönsted: *J. Chem. Soc.*, 574 (1921).

[29] Harned and Akerlöf: *Trans. Faraday Soc.*, **24**, 666 (1928).

[30] Harned: *J. Am. Chem. Soc.*, **40**, 1461 (1918).

[31] Bowe: *J. Am. Chem. Soc.*, **31**, 290 (1927).

[31a] Dawson and Key: *J. Chem. Soc.*, 1239 (1928).

The pertinent data for 0.1 N acetic acid, in sodium chloride solutions, are given in the following table:

Neutral salt (NaCl) mols/liter	Velocity $v.10^6$	Catalytic * coefficient for H^+ ion $k.10^4$	$[H^+].10^3$	Ionization constant of acid ~ $K.10^5$ *
..	0.777	4.65	1.35	1.82
0.2	0.975	4.91	1.68	2.82
0.5	1.055	5.30	1.71	2.91
1.0	1.143	5.95	1.67	2.79
2.0	1.180	7.26	1.42	2.02
4.0	1.165	11.10	0.92	0.84

* The contribution of a catalytic agent, C, to the reaction velocity, for a given concentration of the reactant, is generally expressed by $v_C = k_C \cdot c_C$, where c_C is the concentration of this special catalyst. Dawson, consequently, calculates the catalytic coefficient from the slope of the lineal portion of the velocity curve in relation to salt concentration.

It appears from Dawson's table that neutral salts affect the catalytic activity of partially ionized acids in two ways, viz.:

(1) The neutral salt increases the catalytic activity of the hydrogen ion, an effect which increases with increasing salt concentration;

(2) The ionization constant of the acid increases to a maximum and then decreases.

The effect of the neutral salt, at higher concentrations, is likely due to the action of interionic forces, the salt ions being polar. Their positive poles will be nearer to the negative anions and vice versa and, in this way, tend to increase the ionization, up to a certain point. At higher salt concentrations, the neutral salt ions decrease the ionization of the acid, this perhaps being due to polar association effects between the polar salt molecules themselves. In fact, Brönsted has shown that the salt effect strongly affects the activities of the reactants and the critical intermediary reaction complex, especially at substantial salt concentrations. This is very reasonable as the activities depend so much on the ionic strength of the solution.

f. Solvent effects

The solvents, in which the reactants are dissolved, have a very considerable influence on the reaction rates, as will be shown by some examples.

Lowry divides solvents, in acid-base catalysis, into three groups as to their chemical nature:[32, 33]

(a) Amphotheric solvents which act as complete catalysts, i.e., the solvent is both a proton donor and a proton acceptor.
(b) Solvents which are either acids or bases. These solvents are, in themselves, no catalysts, but they act in the presence of auxiliary catalysts.
(c) Inactive solvents which are neither acids nor bases.

The forces, acting in solvents between polar molecules, have been called collectively *force of cohesion* by van der Waals, or *molcohesion* by K. H. Meyer and H. Mark. These forces are indirectly measurable from the latent heat of evaporation. The stronger these forces are, the stronger the polar properties of a solvent appear to be. The following table presents the molcohesions in calories per mol of typical chemical groups:[34]

$—CH_3$	1780	—CH—	380	—CHO	4700	—Cl	3530
$=CH_2$		—O—	1630	—COOH	8970	$—NO_2$	7200
$—CH_2—$	990	—OH	7250	$—COOCH_3$	5600		
=CH—		=CO	4270	$—COOC_3H_5$	6230		

Kendall[6, 8] assumes that compound formation, between solvent and solute, is preliminary to ionization. For instance, pure hydrochloric acid and pure water are both almost non-conductive, but the mixture of the two has a high conductivity. This may be due to the following reaction:

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[32] Lowry: *J. Chem. Soc.*, **127**, 1371, 1385 (1925); *ibid.*, **129**, 2539, 2554 (1927).

[33] Skrabal: *Ibid.*, **24**, 692 (1928).

[34] Jordan, O.: *The Technology of Solvents*, New York, Chemical Publishing Co., 1940.

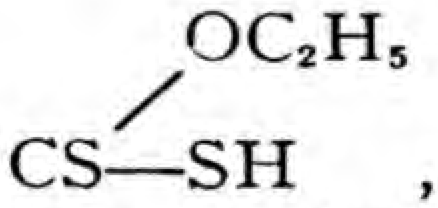
$$H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-$$

Moelwyn-Hughes and Hinshelwood[35] studied the decarboxylation of trinitrobenzoic acid in various solvents. The reaction scheme is:

$$C_6H_2(NO_2)_3COOH \rightarrow C_6H_3(NO_2)_3 + CO_2$$

The velocity constant was calculated by using the equation for the rate of a bimolecular gas reaction, $\ln k = \ln Z - \frac{E}{RT}$, where E is the heat of activation and Z the collision number.

Solvent	E in Calories	ln Z	$k_{60°C} \times 10^{-9}$ Seconds^{-1}
Water	29,970	32.85	3,330
Anisole	30,730	31.13	197
Nitrobenzene (α)	21,700	22.34	27,500
Nitrobenzene (β)	26,320	27.97	6,350
Nitrobenzene (γ)	34,990	33.75	4.07
Acetophenone (α)	24,130	23.00	1,250
Acetophenone (β)	25,450	24.23	579
Toluene	31,600	27.68	1.62

Xanthic acid,  $CS(OC_2H_5)SH$, decomposes into CS_2 and C_2H_5OH, the alcohol acting as catalyst. Halban and Kirsch[36] have shown that the influence of the solvent, on the velocity of this reaction, is tremendous:

	$k_{25°}$	Relative values of $k_{25°}$
CS_2	0.00000132	1.00
Ligroin (hexane)	0.00000198	1.50
Chloroform	0.00000480	3.64
Benzol	0.0000068	5.15
Nitrobenzol	0.000415	315
Ether	0.00064	485
Acetone	0.0343	25,980
Alcohol	(1.3)	1,000,000

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[35] Moelwyn-Hughes and Hinshelwood: *Proc. Roy. Soc. (London)*, **A 131**, 186 (1931).

[36] Halban and Kirsch: *Z. physik. Chem.*, **82**, 325 (1913).

Impurities, in the solvent, also acted catalytically. Similar observations, on catalytic effects of solvent impurities, have been made by Reid[37] and Rice.[38]

Kelber[38a] hydrogenated cinnamic acid in different solvents, using nickel as catalyst. The hydrogenation was fastest in aqueous solvents and aqueous alcohol, i.e., considerably faster than in benzene, acetone, ether, and ethyl acetate. By adding a little water to the organic solvents, especially ethyl acetate, the hydrogenation was speeded up.

g. *Hydrolytic reactions*

The conversion of an ester, into its constituent acid and alcohol, is a hydrolytic reaction which is catalyzed by acids and bases. Usually, this reaction is written:

$$R{\cdot}COO{\cdot}R' + H_2O \rightleftarrows R{\cdot}COOH + R'{\cdot}OH$$

However, in aqueous solution, all proton donors and acceptors act as catalysts in the hydrolysis of esters.[11] Dawson[39] found that OH^-, H^+, CH_3COO^- and CH_3COOH are catalytically active in the hydrolysis of ethyl acetate in acetic acid—sodium acetate mixtures, whereas the catalytic effect of water molecules was negligible.

This leads to the conclusion that, in many reactions, where an acid acts as catalyst, the presence of a base is necessary; and if the base acts as catalyst, the presence of an acid is necessary.[40]

h. *Catalysis in intramolecular changes*

Keto-enol change.[38]

This reaction is depicted by the reaction mechanism:

$$R{\cdot}C(OH){=}CHR' \rightarrow RCOCH_2R'$$

By introducing different radicals for R and R', widely different velocities are obtained, as for instance, there is a considerable difference of velocity in the series ethyl benzoyl acetate, $C_6H_5 \cdot CO \cdot CH_2COOEt$, ethyl aceto acetate, $CH_3CO \cdot CH_2COOEt$, acetyl acetone, $CH_3CO \cdot CH_2COCH_3$, and acetone, CH_3COCH_3. If carefully purified, ethyl benzoyl acetate takes months to attain equilibrium, whereas malonic ester takes only a few seconds.

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[37] Reid, E. Emmet: *Introduction to Organic Research,* New York, D. Van Nostrand Co., 1924.

[38] Rice and Sullivan: *Trans. Faraday Soc.,* **24,** 678 (1928).

[38a] Kelber: *Ber.,* **49,** 55 (1916).

[39] Dawson: *Trans. Faraday Soc.,* **24,** 640 (1928).

[40] Lowry: *Trans. Faraday Soc.,* **24,** 545 (1928).

The rate of the keto-enol change is very substantially affected catalytically, in fact, alkalis are vigorous catalysts, and acids catalyze this reaction too, especially in non-polar solvents. Rice and Sullivan [2, 38] studied the keto-enol change at 250°C in aceto-acetic ester, $CH_3 \cdot CO \cdot CH_2 \cdot COOEt$, calculating the velocity constant, K, by the equation:

$$K = \frac{2.12}{t} \log \frac{X_0 - 0.078}{X - 0.078}$$

X_0 being the initial mol fraction of enol, and X the mol fraction of enol after t hours. The stability of the ester is greatly influenced by slight traces of impurities. By adding different substances in a concentration of 4×10^{-5} to the ester, considerable catalytic effect was obtained:

Catalyst	k_2/K_1*
Piperidine	11,400
Ammonia	4,000
Pyridine	264
Quinoline	17
Bromine	1,300

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* K_1 denotes the rate of change before and k_2 after the addition of the catalyst.
The water content, in the dried ester, was estimated to be 1 part per 1,000,000 parts of ester. Piperidine and ammonia, present in a concentration of N/10,000,000, greatly affect the rate of change. The equilibrium between keto and enol exists in the liquid state (pure substance, or dissolved in solvent) only, solids being either keto or enol.

Tautomerism of α-diketones: [41] Moureu reports that this tautomerism is of the keto-enolic type, one form (A) being one of the possible stereoisomers of the keto-enolic form: $R - CH = C(OH) \cdot CO \cdot R'$, whereas the other form (B) appears to be a true diketone, $R \cdot CH_2 - CO \cdot CO \cdot R'$:

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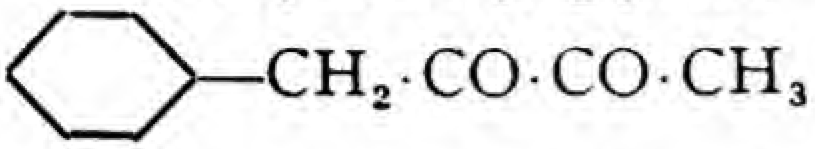
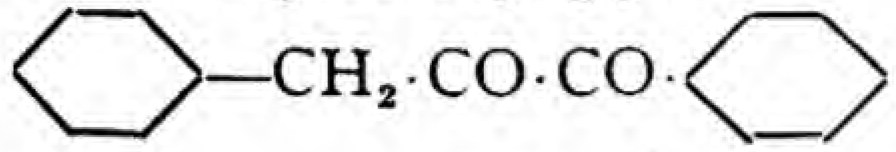
[41] Moureu: *Trans. Faraday Soc.*, **24**, 562 (1928).

	Melting Point ° C	Color
Methylbenzoyl glyoxal  	Form A: 69–70	colorless
	Form B: 17–18	lemon-yellow
Phenylbenzoyl glyoxal  	Form A: 90	yellowish-white
	Form B: 35–36	lemon-yellow

When one of the B-isomers, in a supercooled state, is treated with a trace of alkaline catalyst, it changes into form A. If the temperature (e.g., room temperature) is below that at which the equilibrium: A $\rightleftharpoons$ B exists in a saturated solution of A in B, A crystallizes out and the whole amount of substance is finally converted into this isomer. The rate of change, with different catalysts, is as follows:

Approximate period of the change (Phenyl benzoyl glyoxal)	Conc.	Catalyst	Conc.	Approximate period of the change (Methyl benzoyl glyoxal)
—	—	Benzylamine	1/200	3 days
—	—	Diethylamine	1/200	7 hours
1 hour	1/200	Quinoline	1/200	2 hours
20 minutes	1/200	Pyridine	1/200	45 minutes
—	—	Diethylamine	1/250	A few seconds
A few seconds	1/200	Piperidine	1/250	A few seconds
—	—	Potash	1/1000	12 minutes

Ordinary glass is an active positive catalyst in these conversions, especially in the case of phenyl-benzoyl-glyoxal. If quartz is used instead of ordinary glass, the changes discussed are completely suspended.

In this as in the preceding case, we actually deal with *mixed or simultaneous catalysis*, i.e., homogeneous and heterogeneous catalyses take place simultaneously. There is no doubt that in the course of time a very large number of homogeneous catalytic reactions will be revealed as mixed or simultaneous catalytic reactions.

Mutarotation of sugars: Lowry and Krieble[42] studied the

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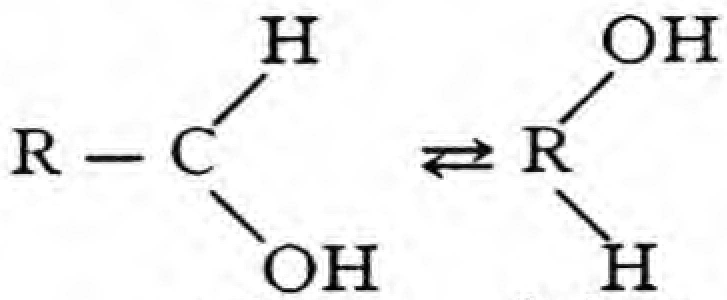
[42] Lowry and Krieble: *Z. phys. Chem., Bodenstein Festband,* 881 (1931).



α-form β-form

mutarotation of galactonic acid and the γ-lactone of this acid, making polarimeter readings at different wave-lengths, in the visible spectrum, in order to judge the complexity of the isomeric changes involved. The equilibrium between the acid and γ-lactone (assuming that no δ-lactone is formed) is 25.2% acid: 74.8% lactone.

The acceleration of the mutarotation, by acids, requires a concentration of about N/100, but the same acceleration is produced by an alkali at a concentration of N/1,000,000. In experiments by Lowry and Wilson[43] the concentration of the OH-ion was derived from $K_H = [OH^-][sugar]/[sugar\ ion^-]$. The acid dissociation constant for lactose was calculated to be $K_A = [H^+][sugar\ ion^-]/[sugar] = 6.0 \times 10^{-13}$. From $K_A \times K_H = Kw$, the catalytic coefficient is derived to be $k_{OH} = (k_e - k_{water}) \times [H^+]/Kw$. In this way, it was found on the basis of electrometric measurements that the catalytic coefficients (k_{OH}) for the following substances are:

Lactose	5,000
Glucose	8,000
Tetramethyl glucose	1,600

It has been established that mutarotation, as described here, requires the presence of both a proton donor and a proton acceptor. Weak acids and their anions and cobalt-amine and chromium-amine cations are catalytically active in this isomeric change, in aqueous solutions, and so is the sulfate ion, as the bisulfate ion is a sufficiently weak acid and the SO_4^{--} ion acts, to some extent, as a base: $H^+ + SO_4^-$.[44]

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[43] Lowry and Wilson: *Trans. Faraday Soc.*, **24**, 683 (1928).

[44] Brönsted and Guggenheim: *J. Am. Chem. Soc.*, **49**, 2554 (1927).

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R. P. Bell: *Acid-Base Catalysis*, Oxford, Clarendon Press, 1941; S. Glasstone: *Recent Advances in Physical Chemistry*, London, J. & A. Churchill, **1931, p. 417.**

15. Heterogeneous (contact) catalytic reactions

In heterogeneous catalytic reactions, the catalyst and the reacting and resulting substances are in different phases. Considering the fact that homogeneous chemical reactions are often sensitive to dust particles and to wall reactions, heterogeneous catalytic reactions are undoubtedly more widespread than is commonly recognized. As heterogeneous reactions take place on a phase boundary, the term phase-boundary catalysts actually is the most adequate one.

There are many kinds of heterogeneous catalytic reactions, and no single reaction mechanism will represent all, but some generalization can be made. Evidence shows that the action of a heterogeneous catalyst is due to (1) residual surface forces (van der Waals forces; chiefly contributing to physical adsorption); (2) molecular forces (liquids); (3) metallic lattices (unsaturated lattice forces; electrons); (4) homopolar forces in atomic lattices; (5) electrostatic forces in ionic lattices.[1, 2]

The type and rate of action, taking place on a contact surface, will essentially depend on:

(1) The nature of the unsaturated forces on the surface of the catalyst;

(2) the nature of the reactive forces of the reacting substances and of the solvent if such is used;

(3) the adsorption, spatial arrangement, deformation, and, perhaps, isomerization of the reactants on the contact surface;

(4) the free energy decrease and the heat of formation in the chemical reaction taking place on the surface of the catalyst;

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[1] Sauter: *Kolloid Z.*, **46**, 148 (1928); *ibid.*, **49**, 450 (1929).

[2] Sauter: *Z. Electrochem.*, **36**, 874 (1930).

(5) the time of contact of the reaction products;
(6) the temperature and pressure (in gas processes);
(7) side reactions.

In the successive stages of a chemical reaction, in which heterogeneous catalysis plays a part, the contact surface takes the part of the reaction sphere in homogeneous catalysis (see page 62), and virtually also of the intermediate compound.

a. Phases

Schwab[3] classifies heterogeneous catalytic reactions according to the state of aggregation of the contacting phases:[1, 2, 3]

	Substrate	Catalyst	Frequency of occurrence
A. Catalyst of higher or same density as substrate.	1. Gaseous	Liquid	Rare
	2. Gaseous	Solid	Very common reaction
	3. Liquid	Liquid	Rare in heterogeneous reactions
	4. Liquid	Solid	Very common reaction
	5. Solid	Solid	Rare
B. Catalyst of lower density than substrate.	6. Liquid	Gaseous	Rare
	7. Solid	Gaseous	Rare
	8. Solid	Liquid	Rare

In judging equilibria between allotropic modifications, the phase rule applies. Iron, for instance, exists in three allotropic forms:[4]

α—ferrite; stable below 900°C
γ—ferrite; stable between 900 and 1400°C
δ—ferrite; stable above 1400° C

In preparation of alloy catalysts and in interpreting high-temperature catalysis, phase rule studies deserve more attention from a catalytic point of view than was given them up to the present time.

Nickel exists in two allotropic forms,[5] cubic and hexagonal:

$$\text{Hexagonal nickel} \rightleftarrows \text{Cubic nickel}$$

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[3] Schwab, G. M., H. S. Taylor, and R. Spence: *Catalysis from the Standpoint of Chemical Kinetics,* New York, Van Nostrand Co., 1937.

[4] Findlay, A.: *The Phase Rule and Its Applications,* London, Longmans, Green and Co., 1933.

[5] Le Clerc and Michel: *Compt. rend.,* **208,** 1583 (1939).

this equilibrium existing in the temperature range of 170 to 250°C, which is a range of temperature very important for the preparation and use of nickel catalysts.

b. Adsorption

In order to understand the nature of adsorption, the following typical cases should be noted:[6] (1) Physical adsorption by secondary valences (van der Waals' adsorption) comprehends adsorption of a gas or vapor by a solid at low temperature. This adsorption is completely reversible, and equilibrium is very rapidly attained. (2) Activated adsorption takes place at higher temperatures than that of (1), and equilibrium is reached more slowly. The velocity of this adsorption is characterized by a temperature coefficient from which an apparent energy of activation can be calculated. (3) Chemisorption is due to formation of a chemical compound between an adsorbed gas and a contact surface. In this case, the gas is not recoverable by exhaustion alone. To this should be added[7] diffusion of gases into or through metals and other substances, especially at higher temperatures.

It is generally agreed that the mere physical adsorption of gases, vapors, and liquids, on contact surfaces of no specific chemical activity, e.g., carbon and silica gel, is not sufficient inducement for chemical activity. In order to become chemically reactive, the contact surface must possess those specific properties which we commonly call the activity of the catalyst. This is a property which experience has shown to be specific for the catalytic reaction in question. However, the adsorption of the reactants, on a catalytically active contact surface, is a matter of great importance as the reactants, in this way, are brought close together (concentrated) and in proper spatial position. A catalytically active contact surface acts chemically in the formation of atoms and radicals of very high reactivity, creating favorable conditions for chemical combinations.

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[6] **Griffith, R. H.:** *The Mechanism of Contact Catalysis,* Oxford, Oxford University Press, 1936.

[7] **Balandin:** *Z. physik. Chem.,* **B 2,** 289 (1929); *ibid.,* 3, 167 (1932).

Adsorption Isotherms

A frequently used adsorption isotherm, especially applicable in representing physical adsorption, is the one proposed by Freundlich, which for gases on solids is expressed as:

$$\frac{x}{M} = Kp^{\frac{1}{n}}$$

where x is the amount of gas absorbed, M is the size of the surface, and p is the pressure of the gas. K and n are constants for the contact surface and the gas, although of empirical nature only.

On the basis of detailed experimental observations and data, Langmuir[8] developed his adsorption isotherm which is very useful in the study of contact surfaces reacting with gases. The number of gram molecules of a gas, which strikes one square centimeter contact surface per second, is given by

$$\mu = \frac{43.74 \times p}{\sqrt{MT}}$$

where μ, for a given gas at constant temperature, is proportional to the pressure, p, M is the molecular weight of the gas, and T is the absolute temperature. If a fraction, a, of the molecules strikes the surface, $a\mu$ gram molecules condense on the surface per square centimeter and per second. When the surface reaction is in equilibrium with the surrounding gas, the rates of condensation and evaporation of gas molecules is equal. At this point we have:

$$(1 - \theta) a\mu = \nu\theta \text{ and}$$

$$\theta = \frac{a\mu}{\nu + a\mu} \text{ (Langmuir's isotherm)}$$

where θ denotes the fraction of the contact surface covered with gas molecules at any moment, and consequently $(1 - \theta)$ the part of the surface on which no gas molecules are adsorbed. Thus, it is seen that the rate of condensation in this case is equal to $(1-\theta)\alpha\mu$; and the rate of evaporation is proportional to the area covered with condensed gas molecules, i.e., to $\nu\theta$ per second, where ν is a constant depending on the gas and the surface.

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[8] Langmuir: *J. Am. Chem. Soc.*, **40**, 1361 (1918); ***Trans. Faraday Soc.*, 17**, 1 (1921) (Reprint).

It has more recently been pointed out by Langmuir[9] that the physical assumptions underlying the factor $(1-\theta)$ are very improbable, because experiments on the adsorption of cesium vapor by tungsten proved that all the cesium atoms striking the surface, even at high temperature, condense, although the surface may be covered as much as 98% with adsorbed cesium atoms. It is deduced that the atoms, incident on the surface, move to vacant sites because of surface mobility, and that it would be reasonable to replace the term $(1-\theta)$ with $(1-\theta^4)$.

Heterogeneous Catalytic Mechanisms

As for the adsorption isotherms, absolute generalizations can not be made, but some examples are very illustrating.

A single gas in contact with a solid catalyst surface: According to Langmuir,[8, 9, 10] the rate of condensation of the reacting gas on a sparsely covered surface is equal to $\alpha\mu$, and the rate of evaporation is equal to $\nu_1\theta^n$, where n is the number of elementary spaces occupied by each molecule of the reactant while in contact with the surface, and ν_1 is a constant determining the rate of evaporation. Consequently, at equilibrium, we have:

$$\alpha\mu = \nu_1\theta^n$$

Considering that chemical reaction takes place by molecules or atoms from m adjacent spaces, the rate of reaction is:

$$\frac{dx}{dt} = \nu_2\theta^m$$

where ν_2 is a constant which determines the rate of evaporation of the new substance formed on the contact surface. ν_1 and ν_2 being constants and μ proportional to the gas pressure, the rate of the reaction is expressed by:

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[9] Langmuir: *Chem. Revs.,* **13,** 147 (1933); *J. Chem. Soc.,* 511 (1940) (Reprint).

[10] Glasstone, S.: *Recent Advances in Physical Chemistry,* London, J. and A. Churchill, 1931, p. 322.

$$\frac{dx}{dt} = kp^{\frac{m}{n}}$$

where k is a constant.

When hydrogen dissociates on a tungsten filament, m/n is equal to 0.5, which gives $n = 2$, i.e., the hydrogen molecule occupies two elementary spaces on the surface of the tungsten and as $m = 1$, the two resulting hydrogen atoms each come from one elementary space. When hydrogen atoms combine on the tungsten, m/n was found to be equal to 2, and $m = 2$, and $n = 1$, the conclusion being that two adjacent hydrogen atoms combine to form a molecule, H_2. The rate of dissociation of hydrogen, on a tungsten surface, is $dx/dt = kp^{0.5}$, indicating that the order of the reaction is 0.5. This actually is due to the fact that one molecule condenses on two elementary spaces on the surface and the reaction is unimolecular.

Decomposition of gases and vapors offers examples for this type of reaction (NH_3; N_2O; CH_3CHO).

Two reacting gases in contact with a solid catalyst surface.[10] When two reacting gases are in contact with a catalytic surface, which is a quite common process, the following possibilities have to be considered:

1. One of the reactants may be adsorbed to a slight extent.
2. Both of the reactants adsorbed to a slight extent.
3. The surface saturated with one of the reactants.
4. The catalyst surface is poisoned by strong preferential adsorption of the substances resulting from the reaction.

Furthermore, it must be considered that the probability of reaching the surface is greater for one than for another reactant, and that combination only occurs between molecules adsorbed adjacently. Thus, if the reactants are A and B, the rate of reaction is:

$$\frac{dx}{dt} = k\theta_1^x\theta_2^y$$

where θ_1 and θ_2 are the fractions of the surface on which A and B, respectively, are adsorbed, A being adsorbed on x spaces, B being adsorbed on y adjacent spaces, and k being a constant.

If the number of reacting molecules of A is $a = \frac{x}{n_1}$, and those of B is $n = \frac{y}{n_2}$, then

$$\frac{dx}{dt} = Kp_A^a p_B^b$$

where p_A and p_B are the partial pressures of the gases A and B, respectively.

If one of the reactants, A, is preferentially adsorbed on the catalytic surface, covering the surface almost completely, reaction will occur whenever a molecule of B condenses on the surface left free by A, and the rate of the reaction will be:

$$\frac{dx}{dt} = \frac{Kp_B}{(p_A)^{\frac{n_2}{n_1}}}$$

If the reaction product is preferentially adsorbed, as in the case of SO_3 in the oxidation of SO_2 on platinum: $2SO_2 + O_2 \rightleftarrows 2SO_3$, by[11, 12] using an excess of SO_2, the surface will be chiefly covered with this gas, and the rate of reaction will be proportional to the partial pressure of the oxygen, i.e.,

$$\frac{dx}{dt} = K\frac{[O_2]}{[SO_3]^{1/2}}$$

Activated Adsorption

Whereas ordinary physical adsorption is greatest at low temperatures where heterogeneous catalytic reactivity is low, other ad-

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[11] Bodenstein and Fink: *Z. physik. Chem.*, **60**, 1, 46 (1907).

[12] Taylor and Lenher: *Z. physik. Chem.*, Bodenstein Festband (1931).

sorption phenomena occur at high temperatures with high heats of adsorption. The adsorption of hydrogen[13] occurs in two ways, viz., (1) van der Waals' adsorption, occurring rapidly, with low activation energy; (2) adsorption with relatively high activation energies and involving a definite adsorption of the activated molecule. Two contact surfaces were studied: (1) manganous oxide, and (2) a mixture of manganous and chromium oxide having a higher specific activity. At –78°C, the adsorption of hydrogen on manganous chromium oxide is small, rapidly attained, and practically reversible by evacuation at room temperature. At 0°C, the adsorption of hydrogen is smaller and extremely slow.

At 100°C and up to 305°C where van der. Waals' adsorption is negligible, the rate of activated adsorption increases; it is less at 444°C although still substantial, than at 305°C. This adsorption is reversible by reduction of the pressure, e.g., evacuation by continued pumping for long intervals of time at temperatures around 460°C. From the velocities of adsorption at 100 and 132°C, the activation energy of the adsorption can be calculated by:

$$\frac{d \ln v}{dT} = \frac{E}{RT^2}$$

Some data are as follows:

Hydrogen	Areas covered by the adsorbent, cm^2	E in calories per mol adsorbed
	0–10	5,920
	10–15	9,500
	15–20	10,500
	20–25	10,500

Hydrogen		Heats of adsorption, calories per mol
	–78–0° C	1,900
	305–445° C	19,000

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[13] Taylor: *Z. physik. Chem.*, Bodenstein Festband (1931).

Activated adsorption was also studied for oxygen adsorbed on silver at different temperatures.[13]

A very good example of these phenomena is given by Morozov[14] in a study of adsorption of hydrogen on catalytic iron surface prepared by reduction of the oxide. Hydrogen was adsorbed in increasing amounts up to about 90°C, the activated adsorption increasing rapidly and is practically instantaneous at about 200°C. Three different types of processes were definitely established: 1) van der Waals' adsorption predominant up to above 10°C; 2) activated adsorption at a rapid rate above about 30°C and highest at about 100°C; and 3) diffusion at a slow rate from about 120°C up to above 400°C. The activation energy for the activated adsorption is about 20,300 calories per mol, and for the diffusion, about 8,500 calories per mol.

c. Desorption

The removal of the substance or substances, resulting from the reaction on a catalytic contact surface, is probably the slowest and most difficult step in the heterogeneous catalytic reaction mechanism. Consequently, the rate of this removal, which is termed desorption, is one of the major factors in determining the rate of reaction of the process as a whole.

The desorption process can be derived from the rate of dissolution of a solid crystal as expressed by:[15, 16, 17, 18]

$$1. \quad \frac{dc}{dt} = KS(c_\infty - c)$$

where K is the dissolution constant, S is the area of the boundary surface, $c\infty$ the saturation concentration of the dissolved substance in a layer around the dissolving crystal and c the concentration in the liquid phase. K is dependent on the coefficient of diffusion, D, and the thickness of the saturated film, l, K = D/l.[19]

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[14] Morozov: *Trans. Faraday Soc.*, **31**, 659 (1935).

[15] Brunner: *Z. physik. Chem.*, **47**, 56 (1904).

[16] Nernst: *Ibid.*, **47**, 52 (1904).

[17] Noyes and Whitney: *Ibid.*, **23**, 689 (1897).

[18] Wagner: *Ibid.*, **71**, 401 (1910).

In order to approximate the conditions on the surface of a contact catalyst some modification of the above concept is required.

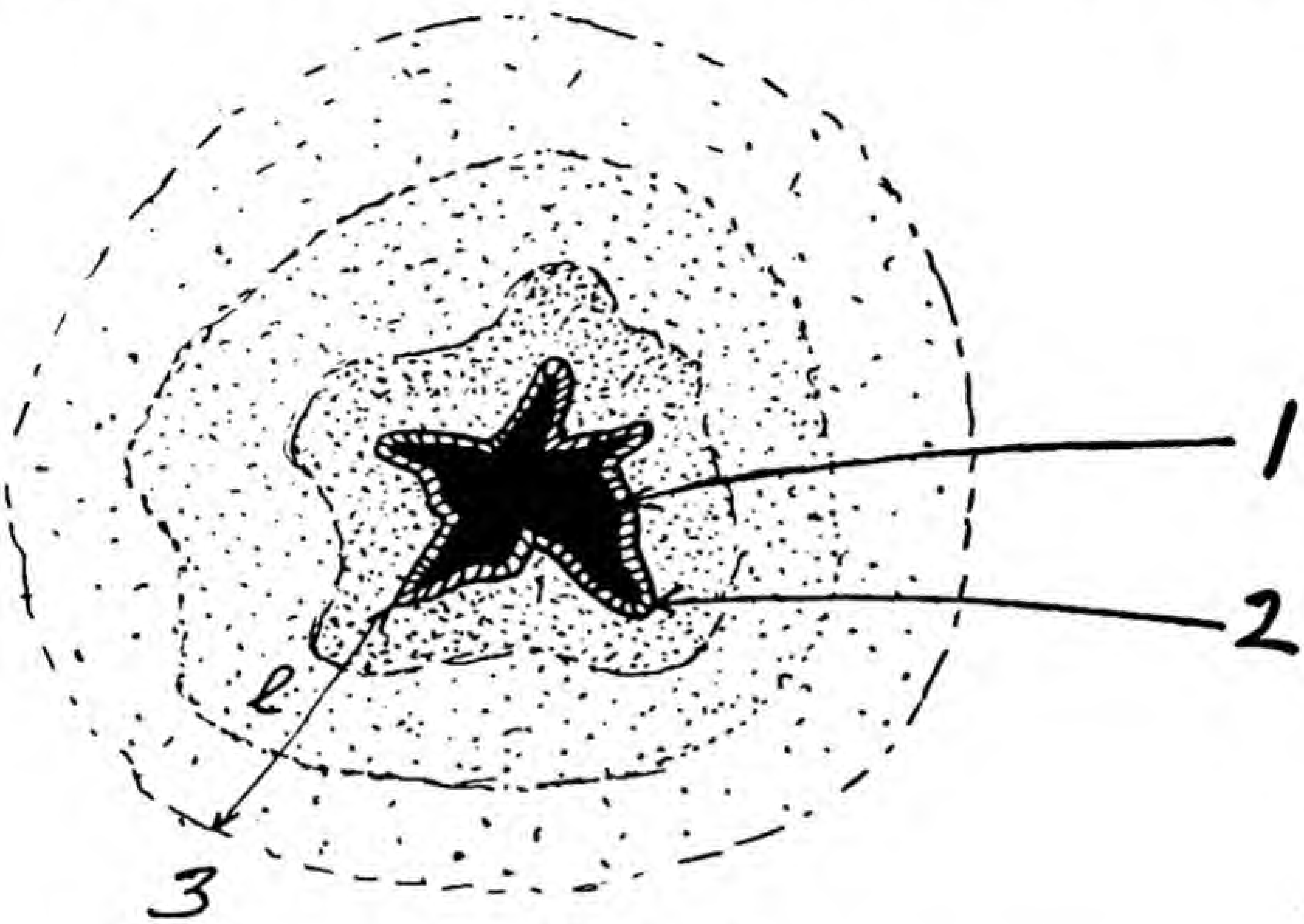

FIGURE 6
SCHEME OF DESORPTION MECHANISM

1. Catalyst particle. 2. Monomolecular layer of reactants and resultant(s). 3. Concentration gradient (l) between monomolecular layer and surrounding medium.

The layer of reactant or reactants and resultant or resultants of a chemical reaction on a catalytic contact surface is considered to be a monomolecular layer, and it appears to be correct to consider this layer as the surface layer of the desorbing contact. However, as catalysis does not take place if the entire monomolecular layer is covered with the resultant, instead of S we will introduce θ from Langmuir's adsorption equation.* l designates the thickness of the layer representing the concentration gradient between the monomolecular layer and the concentration, c, of the resultant in the bulk of the medium at any time, t. D is, therefore, the coefficient of diffusion for this concentration gradient. c_∞ is average concentration in the concentration gradient. Finally, it must also be taken into consideration that under given physical conditions (temperature, pressure, nature of surrounding medium), the contact surface and the resultant possess a specific mutual affinity, h, and furthermore, in exothermic processes, the heat of formation, H, has an accelerating effect on the desorption,* this factor being of the order of H/h. The rate equation (1) for dissolution in this way becomes an equation for rate of desorption:

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[19] Gapon: *Z. Elektrochem.*, 34, 803 (1928).

* $\theta \mp$ area on surface covered with reactants.
$(1 - \theta) =$ area covered with resultants.

$$2.\quad \frac{dc}{dt} = \frac{D}{l}\,\frac{H}{h}\,\theta\,(c_\infty - c)$$

As D/l is constant for a given temperature, we have:

$$3.\quad \frac{dc}{dt} = K\theta\frac{H}{h}(c_\infty - c)$$

where c and c_∞ are values as explained above.

d. Activity

The activity of a catalytic contact surface is judged experimentally, directly by testing the rate of conversion of a given amount of catalyst under standard conditions and indirectly by estimating various properties of the contact surface.

Bowden and Rideal [20] evaluated the "accessible area" of metallic cathode surfaces, e.g., Ni, by measuring the discharge of hydrogen ions on a cathode of the metal, the activity being given as the rate of evolution of hydrogen divided by the true area of the cathode.

Griffith [6] considers the following factors important in examination of a contact surface:

1. The surface area of the catalyst
2. changes in density
3. chemical changes

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[20] Bowden and Rideal: *Proc. Roy. Soc. (London)*, **A** 120, 59, 80 (1928).

* There may be exceptions in cases of activated adsorption.

4. crystal structure (X-ray examination)
5. surface structure (microscopic; electron diffraction methods).

Hilditch and Armstrong[22] studied the activity of nickel catalysts of various origin and established the important fact that the origin and method of preparation are very significant factors in determining the activity of a catalyst:

	Source of reduced nickel			Reduced nickel		
Nickel compound used	Sp. g.	Bulk g (cc)	Reduction temp. °C	Sp. g.	Bulk g (cc)	Catalytic activity
1. Powdered, fused oxide	6.96	0.35	500	8.14	0.52	none
2. Precipitated hydroxide	5.41	0.87	300 500	7.85 8.18	0.83 0.56	fairly * very little
3. Corresponding oxide	3.04	0.91	300 500	... ...	... ...	fairly very little
4. Oxide on diatomaceous earth	1.63	3.22	500	1.85	2.67	very active

* Fairly active: hydrogenate benzene ring in vapor phase reaction.

The same investigators deposited nickel oxide on diatomaceous earth (14.5% Ni) and reduced in hydrogen at 450–500°C to different degrees. The activities of the progressively reduced catalysts were estimated by hydrogenation of linseed oil at 180°C in the presence of 0.1% Ni in the oil. The data were as follows:

		Catalytic activity	
Reduced Ni content %	Reduced Ni / Total Ni	Hydrogen absorbed in oil; liter/minute	Relative activity
2.88	0.199	0.130	0.280
3.56	0.246	0.159	0.342
5.63	0.389	0.302	0.649
6.45	0.445	0.333	0.716
8.46	0.583	0.456	0.981
10.36	0.714	0.465	1.000
12.06	0.886	0.465	1.000
14.19	0.979	0.445	0.957

These experiments are supported by the observation of Senderens and Aboulenc[23] that a temperature of 420°C is required to obtain complete reduction of nickel.

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[22] Hilditch and Armstrong: *Proc. Roy. Soc. (London)*, **A 99**, 490 (1921).

[23] Senderens and Aboulenc: *Bull. soc. chim.*, *(4)*, **11**, 641 (1912).

Warren, Bowles, and Gilmore[24] test catalysts for hydrogenation of coal by heating a number of separate samples in a current of hydrogen under pressure. The loss in weight, during this treatment, is taken as a measure of the amount of distillable products. This method offers the advantage that a large number of catalysts and procedures can be investigated quickly in a preliminary way. It possesses the disadvantage, as the authors point out themselves, that the properties of the volatile product cannot be determined. The details of the apparatus used are shown in figure 7,[25] and the details of the procedure are well presented in the original paper.

Emmett[27] suggests measurement of surface areas of catalysts and other finely divided materials by measuring the volume of nitrogen or argon which is required to form a monomolecular layer of physical adsorption over the entire "inner" and "outer" surface of a catalyst. Adsorption of nitrogen, at −195.8°C on an iron-alumina-ammonia catalyst and on charcoal at pressures up to 600 mm, shows that the nitrogen is adsorbed according to an S-shaped isotherm on the ammonia catalyst, and according to a Langmuir-type isotherm on the charcoal. Emmett et al.[26, 27] postulate that the S-shaped curve is due to formation of multimolecular layers of the gas on the surface, and that the beginning of the linear portion of the isotherm marks closely the completion of the monomolecular layer and the beginning of the second layer. Values calculated on the basis of this theory and data from experiments show good agreement. Whereas the surface area may be estimated, this method does not measure the specific chemical activity of the catalyst.

Haber and Greenwood[28] suggested to express the activity of

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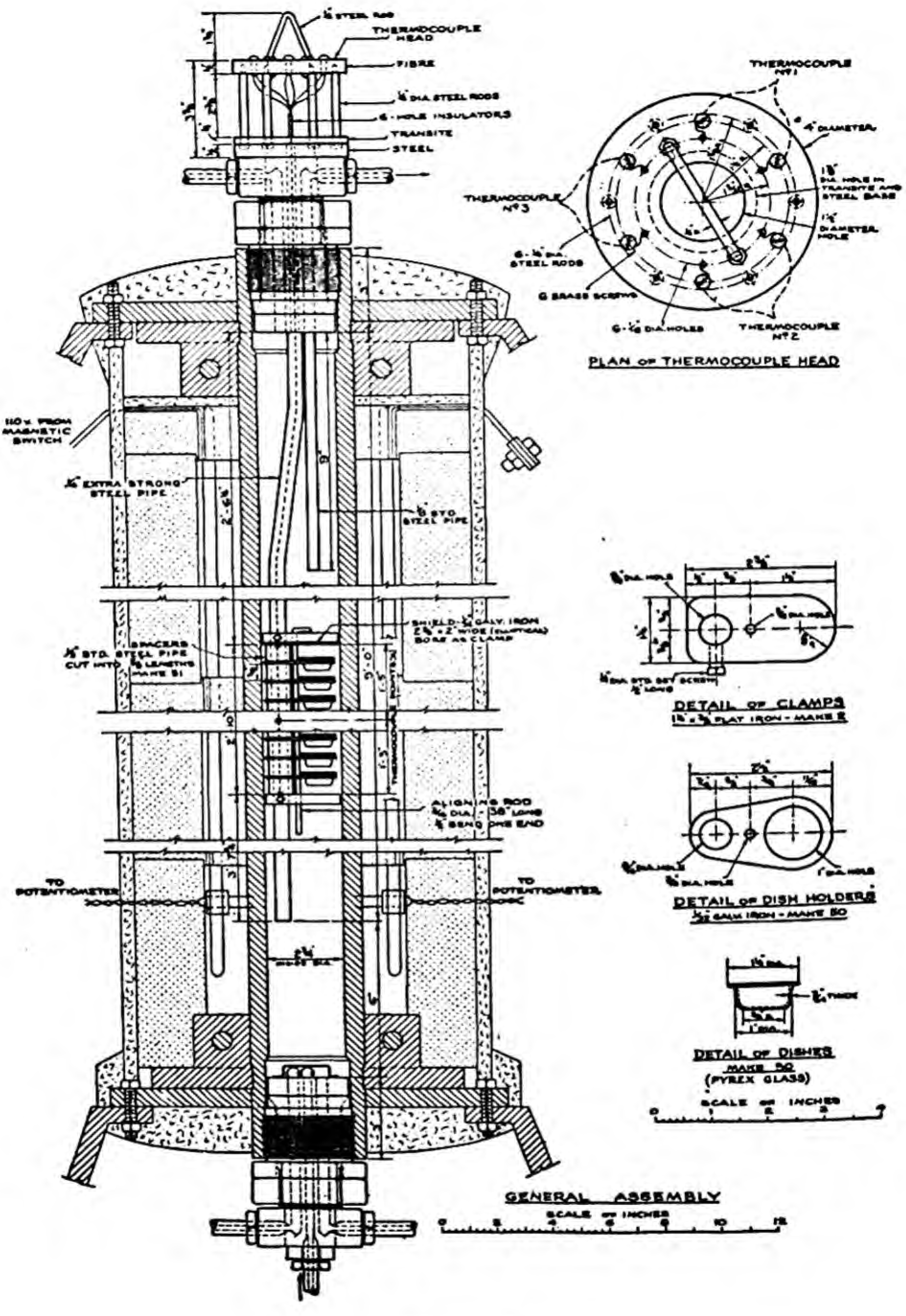
[24] Warren, Bowles and Gilmore: *Ind. Eng. Chem., Anal. Ed.*, **11**, 418 (1939).

[25] Berl and Winnacker: *Z. physik. Chem.*, **A 145**, 161 (1929); *ibid.*, **A 148**, 261 (1930).

[26] Emmett, P. H.: *Physical Adsorption in the Study of the Catalyst Surface.* Twelfth Report of the Committee on Catalysis. New York, John Wiley and Sons, Inc., 1940.

[27] Emmett et al.: *J. Am. Chem. Soc.*, **58**, 1754 (1935); *ibid.*, **59**, 310, 1553, 2682 (1937).

[28] Haber and Greenwood: *Z. Elektrochem.*, **21**, 251 (1915).



STEEL ROD
THERMOCOUPLE HEAD
FIBRE
DIA. STEEL RODS
6-HOLE INSULATORS
TRANSITE
STEEL
THERMOCOUPLE Nº1
4" DIAMETER
DIA. HOLE IN TRANSITE AND STEEL BASE
DIAMETER HOLE
THERMOCOUPLE Nº3
6 - DIA. STEEL RODS
6 BRASS SCREWS
6 - DIA. HOLES
THERMOCOUPLE Nº2
PLAN OF THERMOCOUPLE HEAD
110 v. FROM MAGNETIC SWITCH
EXTRA STRONG STEEL PIPE
STD. STEEL PIPE
SHIELD - GALV. IRON 2" WIDE (ELLIPTICAL) BORE AS CLAMP
SPACERS
STD. STEEL PIPE CUT INTO LENGTHS MAKE 51
ALIGNING ROD DIA. - 38" LONG BEND ONE END
TO POTENTIOMETER
TO POTENTIOMETER
INSIDE DIA.
DIA. HOLE
DIA. HOLE
DIA. STD. SET SCREW LONG
DETAIL OF CLAMPS
FLAT IRON - MAKE 2
DIA. HOLE
DIA. HOLE
1" DIA. HOLE
DETAIL OF DISH HOLDERS
GALV. IRON - MAKE 50
DIA.
THICK
1" DIA.
DETAIL OF DISHES
MAKE 50
(PYREX GLASS)
SCALE OF INCHES
0
1
2
3
4
GENERAL ASSEMBLY
SCALE OF INCHES
0
2
4
6
8
10
12

FIGURE 7

APPARATUS FOR MULTIPLE HYDROGENATION TESTS

(Method by Warren, Bowles, and Gilmore.) (Reprinted by permission from *Ind. and Eng. Chem., Anal. Ed.*, **11**, 418, 1939.)

a catalyst by the space-time yield, i.e., the volume of product which is produced during one hour per unit volume of catalyst.

Laupichler [29] claims that the activity of a catalyst is properly defined by the velocity coefficient of the reaction and its variation with the temperature, and that the experimentally determined values of the velocity coefficient of different catalysts serve as a basis for comparison of their activities.

Pietch and Seuferling [30] have developed a method for estimating the activity of catalysts used for heterogeneous reactions, based on the fact that most of such reactions are exothermic, and they use the heat of reaction as a measure of activity.

Kurbatov [31] incorporates radium and thorium into the catalyst during its preparation and correlates the radon and thoron emanation, under conditions corresponding to the catalytic process, with the catalytic activity. For catalysts, consisting of crystalline particles, the surface areas have been evaluated, and the method is also suggested for study of the stability of catalysts at elevated temperatures and for study of interior surfaces. Kurbatov draws the interesting conclusion that catalysts are not composed of separate, or perfect, crystals, but that the crystals are intergrown and form groupings.

The measurement of catalytic activity for technical purposes is, in the majority of cases, readily accomplished by using a small laboratory converter which simulates, as closely as possible, the reaction conditions in the plant.

e. *Selectivity*

Usually several different reactions may take place. If the temperature is such that they all proceed slowly, the catalyst may speed up one of them selectively. At high temperatures, there is little selectivity. Nickel surfaces act as catalysts in hydrogenation as well as dehydrogenation, the equilibrium favoring the latter at higher temperatures.

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[29] Laupichler: *Ind. Eng. Chem.*, **30**, 578 (1938).

[30] Pietch and Seuferling: *Z. physik. Chem.*, Bodenstein Festband (1931).

[31] Kurbatov: *J. Phys. Chem.*, **45**, 851 (1941).

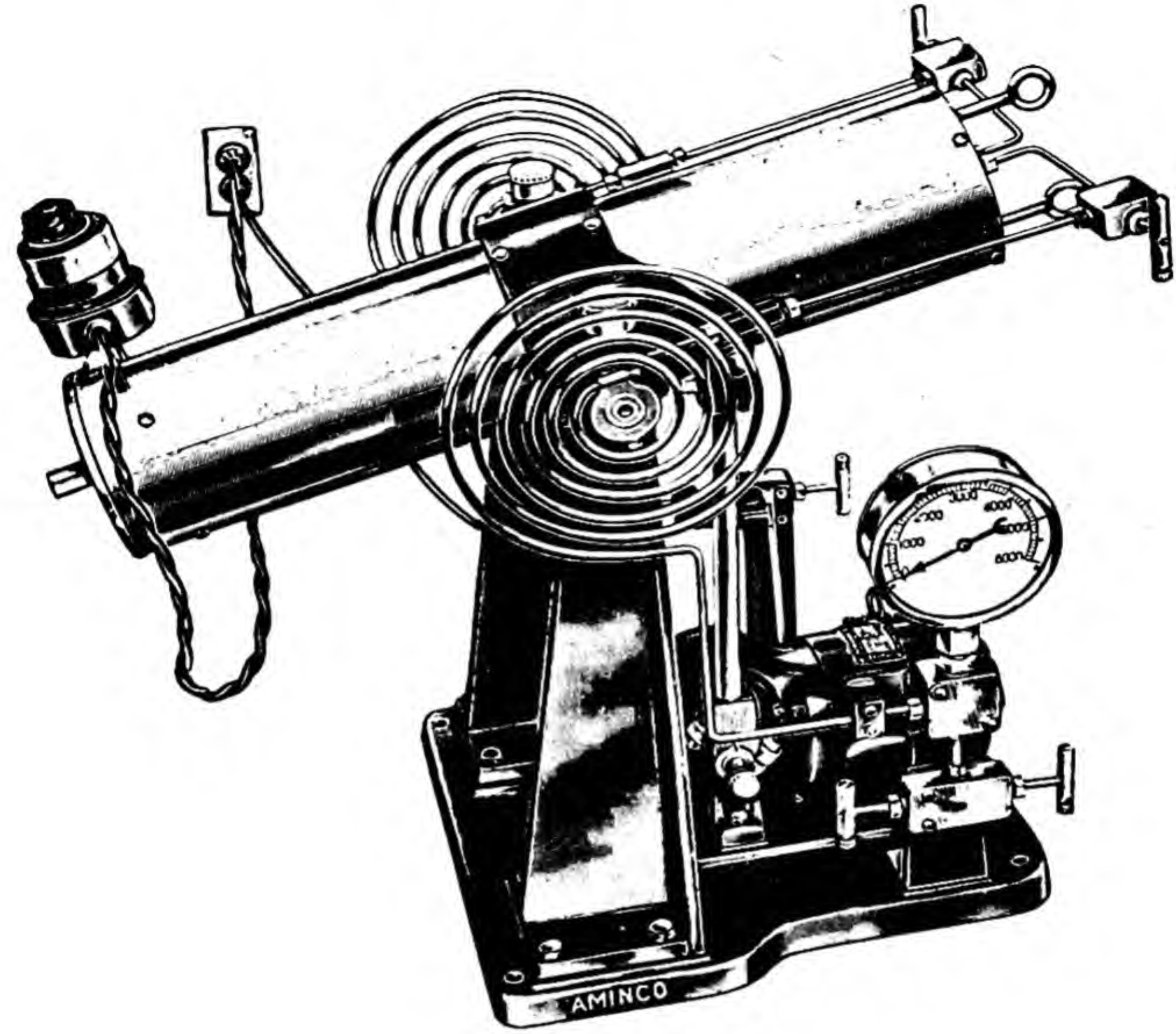

FIGURE 8

High-pressure reaction bomb for laboratory experiments and control work. The bomb is fitted with two pressure connections to provide for continuous flow of hydrogen while the machine is in operation. Bomb pressures up to 703 atmospheres can be used (Courtesy of American Instrument Company, Silver Spring, Maryland).

Selectivity in hydrogenation processes has been studied extensively. It has been shown that nickel is more active with respect to carbon-to-carbon than it is to carbon-to-oxygen double bonds, whereas copper chromite is more active toward carbon-to-oxygen than to carbon-to-carbon double bonds:[32]

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[32] Adkins: *Ind. Eng. Chem.*, **32**, 1191 (1940).

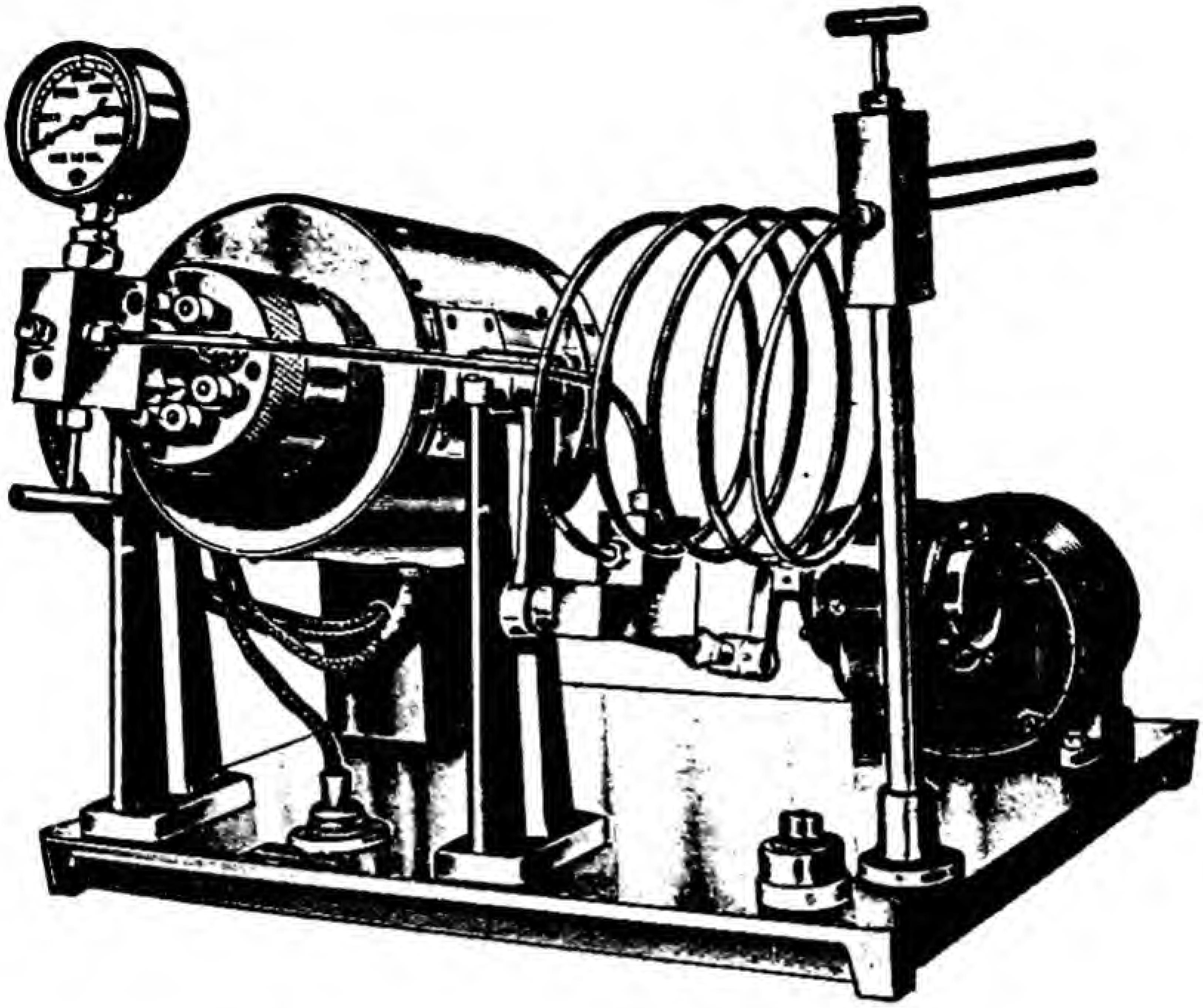

FIGURE 9

High-pressure reaction bomb for hydrogenation reactions of 1 to 300 atmosphere pressure and temperatures up to 400° C; for laboratory experiments and control work (Courtesy of Parr Instrument Company, Moline, Ill.).

Selective Hydrogenation (Adkins)

1. $C_6H_5CH_2CH_2COOEt \xrightarrow[200^\circ C]{Ni} C_6H_{11}CH_2CH_2COOEt$

ethyl β-phenylpropionate — ethyl β-cyclohexylpropionate

2. $C_6H_{11}CH_2CH_2COOEt \xrightarrow[250^\circ C]{CuCrO_4} C_6H_5CH_2CH_2CH_2OH$

γ-phenylpropylalcohol

3. $C_6H_5CH_2CH_2COOEt \xrightarrow[\text{above } 330^\circ C]{\text{Ni or } CuCrO_4} C_6H_{11}CH_2CH_2CH_3$

propylcyclohexane (largely)

Adkins [32] considers this selectivity being due to preferential combination with the catalyst, nickel tending to attach the hydrogen acceptor to itself at alkene or benzenoid linkages, and copper chromite having greater affinity for carbonyl groups as compared to carbon-to-carbon double bonds. The higher the temperature, the less selective is the catalyst, and the more likely it is that saturated hydrocarbons will be formed. Carefully investigated selective hydrogenations have been carried out by Adkins et al.[33] whose publications should be consulted for specific cases.

Olefins (amylene, diisobutene, and octadecene) were selectively hydrogenated by a nickel catalyst in the presence of aromatics (benzene, toluene, and xylene) or n-heptane. Selective hydrogenation was accomplished under superatmospheric pressure and by continuous processing at atmospheric pressure. Using a nickel catalyst from basic nickel carbonate on kieselguhr (containing finally 65% Ni), an activity similar to that of Raney nickel was obtained.[34]

Selective Hydrogenation of Diisobutene
in the Presence of Toluene

Temperature °C	Space velocity, sec	Contact time sec	Ratio H_2/C_8H_{16}	Hydrogenation	
				C_8H_{16}, %	C_7H_8, %
115	1	6	1.5	100	1
125	1	5	1.4	100	1
125	2	3	1.4	100	1
125	3	3	1.4	100	2
150	1	5	1.4	100	1
150	2	3	1.4	100	2
150	3	3	1.3	100	1
175	2	3	1.4	100	1

Mittasch[35, 36] considers that the selectivity of a catalyst is due to (1) selection of a reaction path involving consecutive reactions and/or (2) selection of a parallel alternative reaction. Examples are the different products which are possible by hydrogenation of CO and the further synthesis of the consecutive products obtainable (formaldehyde, methyl alcohol, acids, ethers, esters, aldehydes, ketones, hydrocarbons, cyclic compounds). A classic example of alternative reactions is the dehydrogenation and dehydration of alcohols.

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[33] Adkins, Homer: *Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts,* Madison, The University of Wisconsin Press, 1937.

[34] Ipatieff and Corson: *Ind. Eng. Chem.*, **30**, 1039 (1938).

[35] Mittasch: *Ber.*, **59**, 13 (1926).

[36] Mittasch: *Z. Elektrochem.*, **36**, 569 (1930).

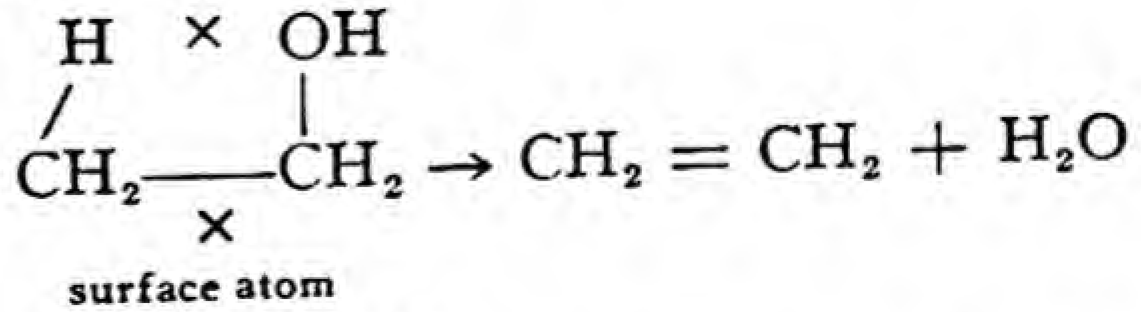
Selective oxidation is frequent in low temperature combustions. Davy[37] showed that hydrogen burns more readily than other combustible gases. Bancroft[38] concluded that the selective oxidation is due to selective adsorption of the gas preferentially oxidized on the catalyst, a view which has been supported by other investigators.

f. Specificity of surfaces

Contact surfaces appear, in some well known cases, to react quite specifically, and it would not be surprising if the mechanism of all reactions on contact surfaces in time were shown to involve such specificities.

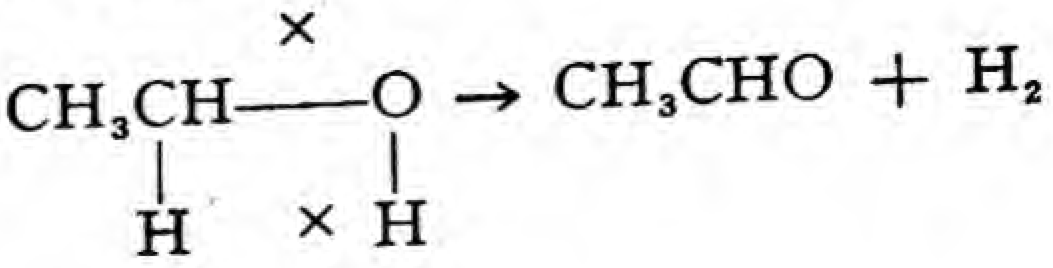
Burk[39] thinks that the contact surface causes a diminution of the heat of activation due to disruption of the molecules by a strain action, which is carried by attachment of neighboring atoms to two different atoms on the surface of the catalyst. If this multiple binding to the catalyst surface produces a strong enough strain, the bond between the atoms is disrupted (multiple adsorption). Balandin[7] proposed a similar mechanism, and added that if two neighboring atoms are attached to the same surface atom on the catalyst, this bond is closed. An example is afforded by dehydrogenation and dehydration of alcohols on different oxide surfaces (multiplet hypothesis):

Dehydration:



$$\underset{\text{surface atom}}{\underset{\times}{\overset{\mathrm{H} \quad \times \quad \mathrm{OH}}{\mathrm{CH_2}\text{——}\mathrm{CH_2}}}} \rightarrow \mathrm{CH_2 = CH_2 + H_2O}$$

Dehydrogenation:



$$\mathrm{CH_3}\underset{\mathrm{H} \quad \times \quad \mathrm{H}}{\overset{\times}{\mathrm{CH}\text{——}\mathrm{O}}} \rightarrow \mathrm{CH_3CHO + H_2}$$

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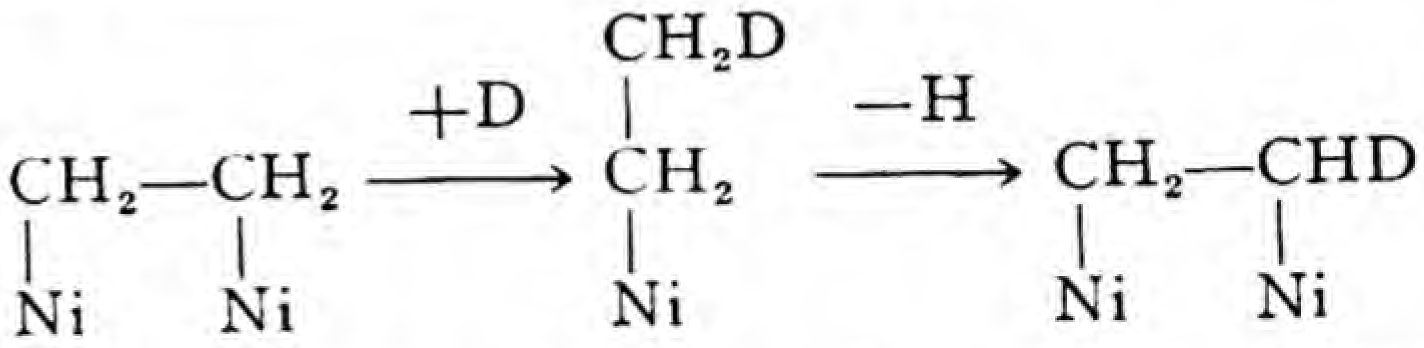
[37] Davy: *Phil. Trans.*, 107, 77 (1817).

[38] Bancroft: *J. Phys. Chem.*, 21, 644 (1917).

[39] Burk: *J. Phys. Chem.*, 30, 1134 (1926).

It should be mentioned that Balandin's theory does not agree with results obtained by Lazier and Vaughan.[40]

Rideal et al.[41] investigated the exchange-reaction between olefins and deuterium and deduced that the exchange proceeds through an association mechanism:



$$\underset{\mathrm{Ni}\qquad\mathrm{Ni}}{CH_2{-}CH_2} \xrightarrow{+D} \overset{CH_2D}{\underset{\mathrm{Ni}}{CH_2}} \xrightarrow{-H} \underset{\mathrm{Ni}\qquad\mathrm{Ni}}{CH_2{-}CHD}$$

The exchange process takes place through the primary addition of a deuterium atom to a chemisorbed ethylene molecule forming an ethyl radical which then decomposes to give a deuterated ethylene molecule and releases a hydrogen atom.

When ethylene is chemisorbed on the catalyst, the double bond is opened, and attachment takes place between the two carbon atoms of the double bond and two nickel atoms. Consequently, the fitting of the olefine to the catalyst surface is an important factor. The following values for the lengths of the bonds are used:

Ni—Ni	2.47Å	(distance of closest packing in the crystal)
Ni—C	1.82Å	
C—C	1.52Å	

It is seen that the Ni—Ni bond is wider than the C—C bond, and it is well imaginable that if the distances of the atoms in the chemisorbed molecule and the contact surface are beyond certain limits of compatibility no activation can take place.

It was also concluded from these experiments that in hydrogenations, the hydrogen molecule adds as a whole to the ethylene and not by atoms. This conception does not concur with the view that catalytic activity is due to isolated active centers on the catalyst surface, a conclusion also arrived at by Maxted et al.[42] It appears that the conception of active centers on the catalyst surface is to be considered from the point of view of exposure to the different crystal planes of the catalyst surface, a view in support of which the experiments by Rideal et al. concur with data obtained by Beeck, Smith and Wheeler.[42a] One possibility, which appears not to have been investigated, is that, in preparing catalysts of particles of near-colloidal or colloidal dimensions, it is reasonable to expect that individual catalytically active particles constitute only a fraction of the total, the remainder being inactive due to coagulation effects, poisoning, sintering and other deactivating factors (Lohse).

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[40] Lazier and Vaughan: *J. Am. Chem. Soc.*, **54**, 3080 (1932).

[41] Rideal et al.: *Proc. Roy. Soc. (London)*, **A 146**, 630 (1934); *ibid.*, **A 171**, 55 (1939); *Trans. Faraday Soc.*, **36**, 53 (1940).

[42] Maxted et al.: *J. Chem. Soc.*, 1900 (1928); *ibid.*, 502 (1933); *ibid.*, 26, 672 (1934); *ibid.*, 393 (1935); *ibid.*, 603 (1937).

The rate at which the hydrogen is brought into contact with the unsaturate and the catalyst determines the velocity of hydrogenation reaction as this determines the rate of diffusion of the hydrogen to the catalytic surface. The rate of the actual combination of the hydrogen and the unsaturate is so fast that it is not measured in the usual experiments (E.E.R.).[43]

Bahr and Bahr[44] studied the mechanism of hydrogenation of carbon monoxide to methane, using nickel as a catalyst. The reaction mechanism arrived at was as follows:

1. $2CO + 2H_2 \rightarrow CH_4 + CO_2$
2. $CO + 3H_2 \rightarrow CH_4 + H_2O$
3. $Ni_3C + 2H_2 \rightarrow CH_4 + Ni_3$
4. $2CO \rightarrow \underset{\text{atomic}}{C} + CO_2$

The primary reaction in the methane synthesis from CO is:

$$Ni_3 + CO \rightarrow Ni_3C + O$$

the liberated oxygen being used in formation of CO_2. The secondary reaction is:

$$Ni_3C + 2H_2 \rightarrow CH_4 + Ni_3$$

In the presence of Ni_3C as catalyst:

$$2CO + 2H_2 \rightarrow CH_4 + CO_2$$

[42a] **Beeck, Smith and Wheeler**: *Proc. Roy. Soc. (London)*, **A 177**, 62 (1940).

[43] **Huber and Reid**: *Ind. Eng. Chem.*, **18**, 535 (1926).

[44] **Bahr and Bahr**: *Ber.*, **61**, 2177, 2465 (1928).

In the presence of metallic nickel as catalyst:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

The mechanism of the formation of Ni_3C is based on the following thermochemical equations:

$$\begin{array}{ll} 1. & 2CO \rightarrow C + CO_2 + 38{,}900 \text{ calories} \\ 2. & Ni_3 + C \rightarrow Ni_3C - 7{,}000 \text{ calories} \\ \hline 3. & Ni_3 + 2CO \rightarrow Ni_3C + CO_2 + 31{,}900 \text{ calories} \end{array}$$

The carbon is atomic when formed on the surface and reacts with the nickel:

$$Ni_{3\,(\text{atomic})} + C_{(\text{atomic})} \rightarrow Ni_3C + 143{,}000 \text{ calories}$$

The temperature conditions are as follows:

Below 270°C: Formation of Ni_3C with decreasing velocity and final cessation.

From 270 to 380°C: Catalytic conversion of CO with Ni_3C as catalyst.

From 380 to 420°C: Ni_3C decomposes.

Messner and Frankenburger[45] investigated the heterogeneous systems $W—NH_3$, $W—H_2$, $W—N_2$, and $W(N)_x—H_2$. In systematic investigations on the adsorption of H_2, NH_3, and N_2 on tungsten (and also on iron and osmium), the nitrogen showed abnormal adsorption properties, which was concluded to be due to chemical reaction of the nitrogen with the tungsten. At low temperature, the nitrogen combines slowly with the metal, but at higher temperatures, the tungsten takes up increasing amounts of nitrogen which it does not give off on cooling. It was concluded that a nitride was formed on the surface. The nitride absorbed hydrogen slowly between 20 and 200°C and it is assumed that a hydrogenation product of the fixed nitrogen resulted. These phenomena were considered partial reactions in the ammonia synthesis which is assumed to proceed as follows:

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[45] **Messner and Frankenburger:** ***Z. physik. Chem.*****, Bodenstein Festband, (1931).**

1. Adsorption of N_2 and H_2 on the catalyst
2. formation of a "nitride" from N_2 and the contact substance on special active places
3. hydrogenation of the "nitride" to the stage of the "imide"
4. further hydrogenation to NH_3
5. Desorption of the NH_3.

g. *Energy of activiation*

In discussing homogeneous reactions, we saw that the molecules must acquire a definite minimum energy of activation, before reaction or decomposition takes place. The same applies to heterogeneous reactions. In the Arrhenius' equation modified to:[10]

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$

E_a, the apparent heat of activation, differs from the true heat of activation, E_t; two cases arise.

1. For a single reacting compound the reaction products of which do not retard the reaction, we have:

$$E_a = E_t - x$$

where x represents the heat of desorption of a gram molecule of the reacting gas.

2. If the reaction is retarded by one of the products, we have:

$$E_a = E_t + x_1 - x$$

where x_1 is the heat of desorption of the retarding gas.

If the contact surface is completely covered with the reactant, $E_a = E_t$.

Mittasch and Keunecke[46] investigated the decomposition of ammonia on mixed molybdenum catalysts, a reaction which is independent of the pressure in the temperature range below 400°C. The heats of activation were calculated according to:

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[46] **Mittasch and Keunecke**: *Z. physik. Chem.*, **Bodenstein Festband (1931).**

$$E = \frac{2.303 \times 1.98 \log \frac{t_1}{t_2} \cdot T_1 T_2}{T_2 - T_1}$$

where t_1 and t_2 denote the time required for evolution of equally large amounts of N_2 and H_2 at temperatures T_1 and T_2.

Metal Added	Heat of activation for a molybdenum content of the catalyst of:				
	0%	20%	50%	80%	100%.
Ni	—	—	—	24,000	—
Co	—	—	—	24,000	—
Fe	about 30,000	26,000	35,000	25,000	—
Cu	—	34,000	36,000	33,000	34,000
W	—	—	38,000	36,000	—
Mn	—	—	—	28,000	—

Kröger[47] studied the reaction $2H_2 + O_2 \rightarrow 2H_2O$ with catalysts of different chemical behavior and found them to fall into three categories:

1. Adsorption catalysis. Silver contact; strong adsorptive capacity for oxygen.
2. Predominantly chemical action on the contact surface by intermediate formation of oxides which again are reduced: Ni, NiO,Cu.
3. Neither oxygen nor hydrogen is adsorbed, entirely chemical action on the surface: Sb. Heat of activation, not depending on the amount of catalyst.

	Amount of catalyst grams	Heat of activation calories
Silver	2	16,100
	4	14,500
	8	13,480
	16	12,400
	32	11,650
	62	10,800
Nickel	2	18,300

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[47] Kröger: *Z. anorg. Chem.*, **194**, 73 (1930).

	Amount of catalyst grams	Heat of activation calories
Copper	16	17,600
	32	13,500
	64	13,500
Antimony	8	13,500 (±5,000)
	16	13,500
	32	13,500

Dohse[48] studied the influence of structure on the heat of activation (Arrhenius) of alcohols of different molecular structure, by decomposition of the alcohols on the surface of bauxite (alcohol → olefine + water).

Alcohol	Heat of Activation	Mol. Weight	B.P.	M.P.
ethyl	31,000	46	78	−114
n-propyl-	28,500	60	97	−127
sec-propyl-	25,500	60	82	−86
n-butyl-	28,000	74	117	−80
iso-butyl-	26,000	74	108	−108
sec-butyl-	24,000	74	100	−89
tert-butyl-	20,000	74	83	+25
tert-amyl-	17,500	88	102	−12

From the characteristic differences in heat of activation, the heats of activation of the various structural groups were calculated. Except for sec-butyl alcohol good agreement was found. A CH_3-group in α-position decreases the heat of activation 5,500 calories, in β-position 2,500 calories, and in γ-position 500 calories.

Clusius[49] studied the decomposition of ethers, with and without catalysis, and found that the heat of activation is much smaller with a catalyst.

In the presence of iodine these decompositions proceed as follows:

1. $CH_3OC_2H_5 \xrightarrow{460\text{–}550°C} CH_4 + CH_3CHO$

$$CH_3CHO \longrightarrow CH_4 + CO$$

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[48] Dohse: *Z. physik. Chem.*, Bodenstein Festband (1931).

[49] Clusius: *J. Chem. Soc.*, 2607 (1930).

$$2.\quad CH_3OCH(CH_3)_2 \xrightarrow{450\text{–}520°C} CH_4 + CO(CH_3)_2$$

$$CH_3OCH(CH_3)_2 \xrightarrow{450\text{–}520°C} CH_2O + C_3H_8$$

$$CH_3OCH(CH_3)_2 \xrightarrow{450\text{–}520°C} CO + H_2 + C_3H_8$$

Decomposition of ethers—Heat of activation, calories

	Catalytic decomposition Iodine as catalyst	Non-catalytic decomposition
Dimethylether	not catalyzed	65,000
Methylethylether	38,000	47,000
Diethylether	34,000	53,000
Methylisopropylether	29,500	—
Diisopropylether	28,500	60,500
Acetaldehyde	32,500	45,500

Finally, attention is called to a proposal made by Kimbal[50] for calculating the free energy of activation.

h. Heterogeneous catalytic chain reactions

Christiansen and Huffman,[51] and Christiansen[52] studied the mechanism:

$$CH_3OH + H_2O \xrightarrow{190\text{–}250°C} CO_2 + 3H_2$$

which is catalyzed by copper.

On the basis of a general theory of chain reactions, the following heterogeneous reaction mechanism was deduced:

1. Total reaction:
   $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$
2. Surface reactions:
   $H_2O + CHO \rightleftarrows COOH + H_2$
   $COOH \rightleftarrows CO_2 + H$
   $H + CH_3OH \rightarrow H_2 + CHO + H_2$

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[50] Kimbal, G. E.: *Recent Developments in the Theory of Chemical Bonds and Reaction Rates,* Twelfth Report of the Committee on Catalysis, New York, John Wiley and Sons, Inc., 1940.

[51] Christiansen and Huffman: *Z. physik. Chem.,* **A 151**, 269 (1930).

[52] Christiansen: *Z. physik. Chem.,* Bodenstein Festband (1931).

By analogous deductions, the decomposition of methyl alcohol, in the absence of water, is calculated to be:

1. Total reaction:
   $CH_3OH \rightarrow CO + 2H_2$
   $2CH_3OH \rightarrow HCOOCH_3 + 2H_2$
2. Surface reactions:
   $CHO + CH_3OH \rightleftarrows COOCH_3 + H_2$
   $COOCH_3 \rightarrow CO + CHO + H_2$
   $COOCH_3 + CH_3OH \rightarrow HCOOCH_3 + CHO + H_2$

The radicals are reactive and start the process over again.

A thermo-neutral reaction chain is obtained in the para-ortho-hydrogen conversion by means of hydrogen atoms, the initial elementary process of which is endothermic, and the concluding elementary process is correspondingly exothermic:[53]

1. $H_2 \rightarrow 2H - 102{,}000$ calories
2. $2H + 2H_{2\text{para}} \rightarrow 2H_{2\text{ortho}} + 2H$
3. $2H \rightarrow H_2 + 102{,}000$ calories

Due to the reactivity of the free hydrogen atoms the rate of 2 determines the velocity. At the temperature of liquid air, charcoal is an active catalyst for this reaction, this catalyst being promoted by adsorbed molecular oxygen. At ordinary temperatures, platinum black catalyzes the reaction.

i. Wall reactions

The reactions, taking place on the walls of reaction vessels, are not as elaborately investigated as they deserve. However, the existence of such reactions is an established fact.

Rumeau[53a] found that the isomeric keto-enol change in acetoacetic ester is rapidly brought about in vessels of soft glass, whereas in quartz or pyrex the conversion is much slower. (Example: Initial enol content in acetoacetic ester = 43 per cent; after 2 hours in quarts tube = 33 per cent; after 15 minutes in ordinary tube = 7 per cent.)

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[53] Bonhoeffer, Farkas, and Rummel: *Z. physik. Chem.*, **B 21**, 225 (1933).

[53a] Rumeau: *Bull. soc. chim.*, **35**, 762 (1924).

An important wall reaction takes place in the cylinders of an internal combustion engine, where knocking occurs if the ignition starts too early during the compression stroke, with the result that the explosion acts against the returning piston. As is well known, tetra-ethyl lead is an efficient agent (anti-knock) to prevent too early ignition, and so are iron penta-carbonyl and other substances (e.g., colloidal metals in the fuel). Bodenstein[54] suggested that the introduction of anti-knocking agents facilitates the breaking of the reaction chains involved in the combustion. This is quite reasonable as it is known that dust particles facilitate the breaking of reaction chains. Some data show that oxides do not have anti-knock effect,[25, 55] although investigations indicate the reverse; this discrepancy is probably due to differences in dispersion of the oxides, finely dispersed oxides being more active.

Upon the supposition that unstable peroxides are intermediate steps in the combustion process in the cylinder, several reaction schemes have been proposed,[56] the one by Egerton[55, 57] being as follows:

1. $O_{2(\text{active})} + \text{Fuel} \rightarrow \text{Fuel}\cdot O_{2(\text{active})}$
2. $\text{Fuel}\cdot O_{2(\text{active})} + A \rightarrow \text{Fuel}\cdot O + \text{Fuel}\cdot O_{(\text{active})}$
3. $\text{Fuel}\cdot O_{(\text{active})} + O_2 \rightarrow A + O_{2(\text{active})}$, etc.
4. If the chain reacts with the wall:

   $\text{Wall} + \text{Fuel}\cdot O_{2(\text{active})} \rightarrow \text{Wall}\cdot O + \text{Fuel}\cdot O$
5. If the chain reacts with a metallic peroxide:

   $MeO_2 + \text{Fuel}\cdot O_{2(\text{active})} \rightarrow MeO + \text{Fuel}\cdot O + O_2$

   $MeO_2 + \text{Fuel}\cdot O_{2(\text{active})} \rightarrow Me + \text{Fuel} + 2O_2$

   $Me + O_2 \rightarrow MeO_2$ (regeneration of peroxide)

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[54] Bodenstein: *Z. Elektrochem.*, **35**, 535 (1929).

[55] Egerton: *Trans. Faraday Soc.*, **24**, 697 (1928).

[56] Moureu and Dufraisse: *Compt. rend.*, **174**, 258 (1922); *ibid.*, **176**, 624 (1923).

[57] Pidgeon and Egerton: *J. Chem. Soc.*, 683 (1932).

A most interesting study on wall reactions by Jorrissen[58] deserves mention. Jorrissen measured the lowest temperatures (°C) at which CO_2 can be detected in the catalytic oxidation of methane on walls covered with thin layers of alkali halides and obtained the following data:

	°C		°C		°C		°C
LiF	170	NaF	180	KF	210	RbF	220
LiCl	360	NaCl	370	KCl	390	RbCl	400
LiBr	360	NaBr	430	KBr	510		
LiI	410	NaI	440	KI	540		

Finally, it should be mentioned that the wall of the converter in commercial equipment often has definite catalytic action, this being due to the action of the components of the wall itself, or due to the action of deposits which form on the wall during operation. For instance, sulfur and hydrogen sulfide react with iron in steel containers to form sulfides, and steam and carbon dioxide to form Fe_3O_4 with iron.[59]

GENERAL REFERENCES

Brunauer, Emmett and Teller: *J. Am. Chem. Soc.*, **60**, 309; Conference on Heterogeneous Catalysis, Moscow, May 13–16, 1940, *J. Phys. Chem. (U.S.S.R.)*, **14**, 1154 (1940); *Chem. Abstracts*, **35**, 3881 (1941); Lunge and Harbeck: *Z. anorg. Chem.*, **16**, 50 (1898); Taylor et al., *J. Am. Chem. Soc.*, **53**, 578, 813; *ibid.*, **55**, 2613 (1933); *ibid.*, **57**, 660, 1251 (1935); *ibid.*, **60**, 362 (1938); *ibid.*, **61**, 503 (1939); *Trans. Faraday Soc.*, **28**, 247 (1932).

C. N. Hinshelwood: *The Kinetic Change in Gaseous Systems*, Oxford, Clarendon Press, 1933, p. 348.

16. Catalysis in solids

Catalysis of a solid by a solid is probably of greater industrial importance than is generally recognized, especially in compounded mixtures. Such catalysis is ascribed to deformation of electron orbits, an explanation which undoubtedly is quite reasonable in many cases.

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[58] Jorrissen: *Chem. Weekblad*, **38**, 170 (1941); *Chem. Abstracts*, **36**, 5694 (1942).

[59] Thomas, Egloff, and Morrell: *Ind. Eng. Chem.*, **31**, 1090 (1939).

An interesting investigation on reactions of solids catalyzed by water vapor, the solids being in the form of dry powders, gave the following results:[1]

Mixture of powder	Reaction products
$BaCO_3 + WO_3$	$BaWO_4 + CO_2$
$BaCO_3 + SiO_2$	$BaSiO_3 + CO_2$
$CaCO_3 + MoO_3$	$CaMoO_4 + CO_2$
$CaO + SiO_2$	$CaSiO_3$
$La_2O_3 + 3SiO_2$	$La_2Si_3O_9$

The solid powders were dried at 500–800°C and treated with dry gases for two hours. The reaction is considered to be due to diffusion through a layer at the point of contact between the reacting particles.

In studying the intermediate states of formation of nickel aluminate from nickel oxide and aluminium oxide in the solid state,[2] mixtures of NiO and α-Al_2O_3 in a 1 : 1 mol ratio were heated to various temperatures between 500 and 1100°C. The samples were X-rayed, and no detectable compound formation was found below approximately 1100°C; at this temperature, crystals of a spinel became apparent and the lines of the original components had practically disappeared. In measuring the solubility of the different preparations by estimating the alumina content in 0.5 N hydrochloric acid extracts after 2 hours extraction, the following results were obtained:

Temperature of reaction of powder mix, °C	Solubility
(α-Al_2O_3	practically insoluble)
below 690	very slight
690–750	sharp maximum in solubility curve
750–900	solubility 2/3 of its value at maximum
(spinel	practically insoluble)

The conclusion drawn is that, since the α-alumina and the spinel are practically insoluble, the solubility of the powders, in various intermediate stages of reaction, is due to the formation of active centers as a result of the surface reaction of the particles of the two powders.

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[1] Jander and Stamm: *Z. anorg. allgem. Chem.*, **190**, 65 (1930).

[2] Jander and Grob: *Ibid.*, **245**, 67 (1940); *Chem. Abstracts*, **35**, 5051 (1941).

In systems in which a solid and a liquid phase coexist, the liquid may act as an accelerator for processes going on in the solid phase, an example being the function of fluxes in removing surface oxides in soldering.

GENERAL REFERENCE

Fischbeck: *Z. Elektrochem.*, **39**, 316 (1933).

17. Catalysis in mixtures

It was recognized by Willstätter [1] that mixtures can have the properties of new chemical compounds. He termed this special property synergism. This term is applied to cases in which both components have the same effect but a mixture of the two is more active than can be accounted for by the sum of the two activities. This phenomenon is explained, physically, as being due to overlapping of atomic field forces. The synergistic action in solids is exerted at places of contact of the different substances, and is, physically speaking, due to the resulting new fields of forces created at the boundary of contact.[2, 3, 4, 5, 6]

The concept of synergism is encountered, to considerable extent, in biochemistry and pharmacology. Thus, Bancroft and Richter [7] assume that drugs stimulate in some low concentration and depress in higher concentrations. The action of drugs is often synergetic. This phenomenon, like antagonism in biological systems, is intimately linked to the colloidal nature of the substrate. Stepp[8] makes the interesting suggestion that the vitamins are plant hormones which, through synergisms and antagonisms, control plant reproduction and growth.

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[1] Willstätter: *Oesterr. Chem. Ztg.*, **32**, No. 13, 1929; G. M. Schwab (H. S. Taylor and R. Spence): *Catalysis from the Standpoint of Chemical Kinetics*, New York, D. Van Nostrand Company, Inc., 1937.

[2] Haber: *Z. Elektrochem.*, **35**, 533 (1929).

[3] Mittasch: *Ibid.*, **36**, 569 (1930).

[4] Mittasch and Keunecke: *Z. physik. Chem.*, Bodenstein, Festband (1931).

[5] Kuss and Keunecke: *Z. Elektrochem.*, **36**, 690 (1930).

[6] Schwab et al.: *Z. physik. Chem.*, **B 1**, 385 (1929); *ibid.*, **B 9**, 265 (1930); *ibid.*, **B 25**, 418 (1934); *Z. Elektrochem.*, **35**, 573 (1929); *Kolloid Z.*, **68**, 157 (1934).

[7] **Bancroft and Richter**: *J. Phys. Chem.*, **35**, 215 (1931).

Adkins and Diworky[9, 10] hydrogenated pure organic compounds and mixtures, the results being as follows:

Series I Pure compounds. Order of decreasing rate of hydrogenation	Series II Two component mixtures. Decreasing saturation of hydrogen in any mixture
Quinoline	Quinoline
Benzene	Pyridine
Toluene	Aniline
Phenol	Benzylalcohol
Benzylalcohol	Phenol
Pyridine	Diphenylamine
Diphenylamine	Benzene
Acetanilide	Acetanilide
Aniline	Toluene

The hydrogenations were carried out over a nickel catalyst at temperatures from 125 to 175°C and hydrogen pressures from 125 to 200 atmospheres. The mixtures were allowed to take up as much hydrogen as would be required to completely hydrogenate one of the components, and the rate of absorption of hydrogen and its distribution between the two components of the mixtures was determined analytically. It was found that pyridine and quinoline in such two-component mixtures absorbed all, or practically all, of the hydrogen. By comparison between the two series it is seen there there is no correlation between the relative rates of hydrogenation of these compounds hydrogenated singly in the pure state and in two-component mixtures.

18. Periodic reaction changes

A detailed study of the data presented in studies of reaction phenomena reveals the fact that the smooth curves, usually drawn, represent a true picture of continuity only if a very large number of observations or continuous recording is used. However, very often ordinary graphic presentation, or its mathematical equation, is presented on the basis of comparatively few observations only.

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[8] Stepp: *Ernährung*, 1, 26 (1936); *Chem. Abstracts*, 30, 3856 (1936).

[9] Adkins and Diworky: *J. Am. Chem. Soc.*, 53, 1868 (1931).

[10] Adkins, H.: *Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts*, Madison, The University of Wisconsin Press, 1937.

Ostwald[1] registered continuously the changes occurring when metallic chromium is dissolved in dilute mineral acid and made a considerable number of observations on the activation of this metal when dissolved in acids. For instance, a sample of chromium metal was inactivated by oxidizing agents such as potassium permanganate, chromic acid, and oxygen from the air. Strongly reducing agents regenerated the activity, and so did contact with zinc, cadmium, and iron. By measuring the pressure caused by the evolution of the gas, the curves obtained presented minima and maxima, the regularity of which depended on the purity of the acid and addition of various compounds to the acid.

In an experiment with dissolving metallic chromium in an excess of hydrochloric acid, the oscillation readings were as follows:

Chromium-D in 100 cc 2 *N* HCl at 100°C:

110	107	110	115	117	120	104	118	118	113	118
121	124	120	118	124	115	116	115	116	112	121
118	114	114	117	110	110	116	119	115	112	120
110	109	110	111	108	101	101	104	102		

A great number of such periodicity phenomena has been discussed also by Hedges and Myers,[2] and Veil.[3] The former concluded that supersaturation of the liquid, with the gas, is not the cause of the periodic effects, but that the reaction was catalyzed at regular intervals of time, and they found that colloids or a second metal could induce periodic (or pulsating) catalysis. The metals were most effective when a clean crystalline surface, particularly an electrodeposited metal, was exposed.

In order to interpret periodic reaction phenomena, the true chemical composition (purity) of the reaction systems should be completely accounted for. Until that is done, it seems, in view of the preceding discussion (see page 10), that there is not sufficient basis for interpreting such data exactly. The possible catalytic action of impurities distributed throughout a metal or other substance is of high enough probability to account for the periodic appearance and disappearance of a catalytic agent in the reaction taking place between a metal and an acid, and for that matter in other reactions as discussed by the authors cited. To what extent this is true, the future will decide.

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[1] Ostwald: *Z. physik. Chem.*, 35, 33, 204 (1900).

[2] Hedges, E. S. and J. E. Myers: *The Problem of Physico-Chemical Periodicity*, London, Edward Arnold & Co., 1926.

[3] Veil, S.: *Exposés de chimie générale et minérale, III, IV*, Paris, Hermann & Cie., 1934.

CHAPTER III

NATURE AND PROPERTIES OF CATALYSTS

Introduction

It is most likely that any chemical compound can act catalytically under some circumstance or other. Consequently, any discussion of catalysts requires definition and limitation.

Catalytically active substances can be divided into two major groups:

1. Well defined chemical compounds which in the catalytic reaction mechanism react according to a well defined reaction scheme, their special action in catalysis mostly being the formation of a labile intermediary compound. The preparation of such compounds is a problem of ordinary preparative chemistry and does not require special discussion. This type of catalyst is commonly encountered in homogeneous catalysis, examples being the halogens, organic catalysts, and inorganic and organic acids, bases and salts.

2. Contact masses, such as used in heterogeneous catalytic reactions (see page 81), are the substances we usually think of when we speak about the properties and nature of catalysts. This type of substances will be discussed in this chapter.

Although the literature on the subject is tremendous, it must be said that the preparation of a catalytic contact material still is an art more than a science. Furthermore, chemical composition alone is not a sufficient guide in determining the quality of a contact substance because its physical condition is also of vital importance for its activity as a catalyst. Whereas the chemical character of a contact catalyst largely determines the specific type of reaction in which it can be used, the physical condition determines, to a considerable extent, its activity. Generally, it can be said that the activity of a contact catalyst is determined by the total history of its preparation. It follows from this that standardization of procedures, for the preparation of catalysts, is a matter of utmost importance.

Up to the present time, no fully satisfactory interpretation has been presented of phase-boundary or contact-catalytic reactions. It appears, however, that on the active contact surface, a labile compound of very short existence is formed between the unsaturated surface atoms and those of one or both reactants. The contact surface may react with one reactant forming a labile compound which is reactive with the other reactant; or both of the reactants may form a labile compound with the contact surface, the adjacent surface compounds reacting with each other forming a compound of less affinity to the surface.

There has been much speculation as to the nature of the bonds on contact surfaces. From evidence of explicit experiments, such as reported in the section dealing with surface reactions, it appears that the reactions, taking place on a catalyst surface, are just as specific as are other chemical reactions in gases or liquids. The catalytic contact reaction is characterized by the short life of the labile connection which is formed between the reactants and the atoms of the partly saturated surface lattices. The possibility for and the velocity of any such reaction are then determined by the physical and chemical quality of this lattice structure and the substances reacting in the system. The specificity of such reactions has been discussed elsewhere in this text (pp. 25 and 99).

Of other structural studies, correlating the properties of the different elements with their catalytic functions, may be named the work by Thomas, Egloff and Morrell[1] dealing with catalytic effects of the different metals on paraffin hydrocarbons. The interpretation of their data was made on the basis of the following primary reactions:

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[1] Thomas, Egloff and Morrell: *Ind. Eng. Chem.*, **31**, **1090** (**1939**).

1. Dehydrogenation:

$$C_nH_{2n+2} \rightleftharpoons C_nH_{2n} + H_2$$

2. Cracking:

$$C_nH_{2n+2} \rightarrow C_{n-m}H_{2(n-m)+2} + C_mH_{2m}$$

3. Complete decomposition:

$$C_nH_{2n+2} \rightarrow nC + (n+1)H_2$$

The results for the elements of the different groups of the periodic system are as follows:

Group I: Of the alkali metals, only lithium and potassium were reported and no catalytic effect was observed. Copper is a mild catalyst for complete decomposition of the hydrocarbon into carbon and hydrogen, but films form on the surface of the metal. Copper is also considered a dehydrogenation catalyst of slight activity, although it is apt to crack the hydrocarbon. The position of gold and silver is uncertain, although these metals may not be entirely inactive in these reactions.

Group II: Magnesium favors the complete decomposition of the paraffin hydrocarbons, magnesium carbides occurring as reaction products. Calcium favors mildly the same reaction and the presence of carbides in the reaction products. Zinc is inadequately studied, and so are also cadmium and mercury; it is reported that vapors of the last two favor formation of liquids from methane.

Groups III and IV: These two groups have been most inadequately studied for the cases at hand. No catalytic effects were reported for tin, silicon, and titanium. Aluminum favors complete decomposition, the metal uniting with the carbon to form carbides. It is suggested that thallium and indium should be similarly tested.

Group V: No paraffin reactions reported at the time of the publication of this paper.

Groups VI and VII: Chromium has not been studied as a catalyst with paraffins up to this time (1939), but experience shows that chrome-iron tubes substantially reduce carbon formation in commercial cracking units. Molybdenum and tungsten are practically non-catalytic in their massive state, but as powders, both catalyze complete decomposition with the formation of the corresponding carbides. Tellurium favors formation of olefins, especially in the presence of iodine. Manganese, in the massive state, possesses practically no catalytic properties, and as powder, it forms carbides with the carbon formed by complete decomposition of methane.

Group VIII: Iron, cobalt and nickel all strongly catalyze the complete decomposition of hydrocarbons, nickel being more effective than iron, and nickel and cobalt being about equally active for the decomposition of methane. Cobalt is the most active for the decomposition of liquid paraffins. Carbides are formed under certain conditions. Nickel carbide can be isolated only below 480° C, and cobalt carbide only below 668° C. It is likely that these carbides are formed as intermediate compounds during the catalytic decomposition reaction. Palladium favors the complete decomposition of methane into carbon and hydrogen, although higher hydrocarbons may be dehydrogenated to unsaturated hydrocarbons. However, the latter reaction requires further study. Platinum is less active than palladium, and, when active, it favors complete decomposition, some of the carbon formed combining with the metal.

Remy et al.[2] assume that the affinity of a contact substance for oxygen, and its affinity for and its solvent action on hydrogen, are factors of substantial importance for the catalytic activity of metals of the 8th group in the catalytic reaction between hydrogen and oxygen in contact with one of these metals or one of their binary alloys. The activity of these catalysts depends very much on their being charged with oxygen or hydrogen before the reaction, some of the catalysts being most active when previously charged with oxygen, and some most active when previously charged with hydrogen. This is demonstrated in the following figure in which the numbers indicate the relative catalytic activity in the formation of water in the presence of one of these catalysts: *

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[2] Remy et al.: *Z. anorg. und allgem. Chem.*, **136**, 149 (1924); *ibid.*, **149**, 283 (1925); *ibid.*, **157**, 329 (1926).

* The outside squares indicate the catalytic activities of the pure metals, and the inner squares those of binary alloys (50%:50%), e.g., Ir-Ru alloy precharged with hydrogen possesses a relative activity of 74 in a mixture of Knallgas and hydrogen 1:20.

Precharging with oxygen. Mixture of Knallgas and oxygen 1:40

Precharging with oxygen. Mixture of Knallgas and nitrogen 1:60

					34	Pt	27					
				40	22	Ir	39	38				
			0	0	56	Os	56	22	0			
		37	30	53	26	Pd	35	43	49	35		
	0	35	0	0	0	Rh	20	0	0	61	0	
0	0	25	0	25	11	Ru	14	22	0	25	0	0
Ru	Rh	Pd	Os	Ir	Pt		Pt	Ir	Os	Pd	Rh	Ru
0	34	39	0	74	63	Ru	59	75	53	76	137	0
	22	71	54	28	100	Rh	27	65	100	85	56	
		0	74	20	54	Pd	27	63	65	58		
			51	23	49	Os	9	105	90			
				37	30	Ir	36	0				
					34	Pt	68					

Precharging with hydrogen. Mixture of Knallgas and hydrogen 1:20

Precharging with hydrogen. Mixture of Knallgas and nitrogen 1:80

When catalytic metals are precharged with oxygen, which is held in a state of strong reactivity, water is formed immediately because hydrogen is adsorbed strongly and is converted to a form of high reactivity. This is due to the fact that the affinity of the metals to oxygen is not very strong and in this way, the unsaturated metal surfaces are no more occupied by the oxygen than they can exert a strong activating effect on the hydrogen. The authors think that this activation is due to deformation of the hydrogen, and also of the oxygen. This view was originally proposed by Bodenstein. If the metals are precharged with hydrogen, which is adsorbed very strongly leaving little of the deforming effect of the unsaturated metal surface free to activate the oxygen, very little water is formed.

The metals of the 8th group behave differently regarding adsorption of hydrogen and oxygen. One series of the metals, arranged according to increasing affinity to hydrogen, is: Ru, Os, Pt, Rh, Co, Fe, Ni, Ir, Pd, and another series, arranged according to increasing affinity to oxygen, is : Pt, Pd, Ir, Os, Ru, Rh, Ni, Co, Fe.

In searching for substantiating evidence for understanding the nature of catalytic substances in general, Balandin's[3] work is of interest. He makes the conclusion that the structure of the reactant must fit the structure of the catalyst in order that catalysis can take place. If such is not the case, the reacting molecule is absorbed on a single unsaturated surface spot only and no reaction takes place. As an example, Balandin discusses the dehydrogenation of cyclohexane, C_6H_{12}, to benzene, C_6H_6, in the presence of a platinum catalyst at 150°C. The importance of the catalytic action, in this case, is shown by the fact that in the absence of a catalyst, even at 600°C, no hydrogen is split off from this product. The platinum lattice is cubic face-centred and the cyclohexane forms a regular hexagon, these two substances being symmetrical. On the other hand, according to this theory, all catalysts, on the surface of which the atoms are not distributed in regular triangles, are excluded from this dehydrogenation. Thus, all the metalloids, including graphite and activated carbons, and some metals are excluded as dehydrogenation catalysts for cyclohexane.

Examining a considerable number of compounds, Biltz[4] found that when chemical elements combine, the volume of the compound formed is normally a few per cent smaller than the sum of the atomic volumes.

Oxygen in different compounds possesses very different volumes.

Compound	O-volume	Compound	O-volume	Compound	O-volume	Compound	O-volume
Cu_2O	9.3	CuO	5.3	WO_2	5.3*	Tl_2O_3	3.7
Ag_2O	11.8	AgO	6.5	FeO	4.9*	ZrO_2	3.6*
CO_2	11.3	SiO_2	5.3*	CoO	5.1*	ThO_2	3.2
CrO_3	9.5	NbO_2	5.3*	NiO	4.5*	HfO_2	4.0*
UO_3	10.4	ZnO	5.6	Fe_2O_3	5.4*	CdO	3.1
RuO_4	10.7	HgO	5.4	Fe_3O_4	5.8*	In_2O_3	2.9
OsO_4	10.8	SnO	5.0	RuO_2	5.5		
		PbO	5.3	OsO_2	5.6	Average =	3.4
Average =	10.5	MoO_2	5.3*	IrO_2	5.4		
		Average =	5.4				

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[3] Balandin: *Z. physik. Chem.*, **B 2,** 289 (1929); *ibid.* **B 3,** 167 (1929).

[4] Biltz: *Z. anorg. & allgem. Chem.*, **127,** 34 (1923); *ibid.*, **130,** 116 (1923); *ibid.*, **193,** 321 (1930).

* Other interpretation possible.

Double-linked oxygen in organic compounds, i.e., carbonyl-O, has almost the same volume as free oxygen in oxygen crystals, viz., 10.9 (ketones, aldehydes, CO_2). Alcohol-oxygen and ether-oxygen possess a volume of 3 to 4 cm^3. In the carboxyl group, —COOH, one oxygen has a volume as carbonyl-oxygen and the other as alcohol-oxygen.

Equally-Spaced Oxides of Different Oxidation Stages

(Zero volume of the oxygen = 10.9)

Monoxides

Oxide	Mol.-vol.
MgO	11.3
FeO	12.0
CoO	11.7
NiO	11.0
TiO	11.5

Trioxides

Oxide	Mol.-vol.	Mol.-vol./3
MoO_3	30.7	10.2
WO_3	32.2	10.7
Ti_2O_3	31.3	10.4
Fe_2O_3	30.4	10.1

Pentoxides

Oxide	Mol.-vol.	Mol.-vol./5
V_2O_5	54.8	11.0
Ta_2O_5	55.3	11.1

Dioxides

Oxide	Mol.-vol.	Mol.-vol./2
SiO_2	22.6	11.3
TiO_2	20	10
ZrO_2	21.0	10.5
HfO_2	21.7	10.9
SnO_2	21.7	10.9
MoO_2	20.0	10.0
WO_2	20.2	10.1
NbO_2	22.0	11.0

Tetroxide

Oxide	Mol.-vol.	Mol.-vol./4
Fe_3O_4	44.4	11.1

Titanium oxides

Oxide	Mol.-vol.	Mol.-vol./n
TiO	11.5	11.5
TiO_2	20	10
Ti_2O_3	31.3	10.4

It is interesting to note that there is not a very large decrease in the volume of the oxygen atom with increasing oxygen content in the molecule. In another table, Biltz shows that compounds of different stages of oxidation are of practically equal volume:

Compound	Mol.-vol.	Compound	Mol.-vol.
HgF	25.3	HgF_2	26.3
Ag_2O	32.1	Ag_2O_2	33.2
SnO	21.0	SnO_2	21.7
PbO	23.9	PbO_2	24.9
$PrO_{1.5}$	23.5	PrO_2	23.3
UO_2	25.0	$UO_{2.26}$	25.2
$MoO_{2.67}$	30.9	MoO_3	30.7
Cu_2O	24,3	Cu_2O_2	24.8

The alkali metal ions are of about the same space requirement as the atoms of the nearest inert gas, i.e., the same number and content of electron shells give about the same volume. On the other hand, the charge on the nucleus has not much influence on the space requirement. Data for the different alkali metals in different compounds are as follows:

The volumes of the alkalies in different states and compounds

Alkali-metal ion	Zero	Corresponding inert gas	Hydride (reduced value)	Chloride	Formate (reduced value)	Tetroxalate (reduced value) R = 100 *	Telluride	Metal vol.
Na^+	11.4	12.6	11.3	10.7	10.6	..	19.8	22.9
K^+	21.7	21.6	21.0	21.1	19.5	21	...	43.4
NH_4^+	25.5	.	...	25.9	...	25	...	...
Rb^+	26.5	(26.3)	26.8	25.4	(23.5)	26	...	53.1
Cs^+	33	31.9	32.5	...	33.3	32	...	65.9

* R = vol. of the tetroxalate radical

Another interesting fact is that some crystal lattices can bind other substances without changing volume, some examples being:

$$\text{Vol. } Sb_2O_4 = \text{Vol. } Sb_2O_5$$

$$\text{Vol. } N_2 = \text{Vol. } N_2O$$

$$\text{Vol. } O_2 = \text{Vol. } HFO_2$$

$$\text{Vol. } [CO(NH_3)_6]I_2 = \text{Vol. } [CO(NH_3)]I_5$$

These data are interesting in that they throw light on the nature of compounds and steric phenomena dealt with in catalytic problems.

Before discussing the single metals, attention is called to the fact that the same metal can exist in allotropic forms under different conditions. Due to the fact that such phase studies have not been extended sufficiently to catalytic substances, our knowledge on this matter, at the present, is not as extensive as it should be.

Some examples of such allotropic changes are the following:

1. Iron[5] changes, at about 800°C, from cubic body-centred to cubic face-centred form.
2. Cobalt[6] changes, at 1159°C, from cubic face-centred to close-packed hexagonal form.

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[5] Jeffries and Archer: *Chem. Met. Eng.*, **24**, 1057 (1921).

[6] Hull: *Bull. Am. Inst. Electr. Eng.*, **2**, 1171 (1919).

3. Nickel[7, 8] changes from hexagonal to cubic form, between 170 and 250°C, i.e., in the range where nickel is used extensively for catalytic purposes.
4. Tin[9] below 200°C possesses a tetragonal lattice and is white, shiny and soft, and above 200°C, this metal is rhombic and so brittle that it can be pulverized.

Almost entirely neglected, in catalytic work, are the isotopes (except Deuterium). We speak freely of the catalytic activity of the chemical elements, but we do not realize that chemical elements as conventionally discussed are mixtures of different isotopes, and have also a higher or lower content of minor impurities, all of which contribute to the reactivity of any element or compound, the indications being that this contribution is of substantial magnitude. In consideration of this, the isotopes and impurities are given in parentheses after the elements in the following discussion. It is possible, of course, that the effect of isotypes is the smaller the higher their atomic weight.

The Chemical Elements and Compounds in Catalysis

The classification of the chemical elements, as to their catalytic properties, is probably defective due to the fact that so few observations on catalytic reactions have been made where there is nearly a complete account of the chemical composition of the reaction system, minor constituents included. Furthermore, the same chemical element acts differently in catalytic reactions when present in different compositions and amounts. For reasons such as these, the chemical elements and their compounds are here described in the sequence in which they occur in the periodic system.

Hydrogen (1, 2) * is such an important element in catalytic

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[7] Le Clerc and Lefebvre: *Compt. rend.*, **208**, 1650 (1939).

[8] Le Clerc and Michell: *Ibid.*, **208**, 1583 (1939).

[9] Hodgeman, C. D. and N. A. Lange: *Handbook of Chemistry and Physics*, Cleveland, Ohio, Chemical Rubber Publishing Co., 1929.

* Numbers in parentheses after an element indicate isotopes (compare F. W. Ashton: *Mass Spectra and Isotopes*, London, Edward Arnold & Co., 1933).

studies and the industry that a brief mention of its properties will be useful in a text such as this.

Hydrogen mixes faster with other gases than any other gas and it diffuses through porous bodies and many metals, the latter at temperatures from 300 to 400°C and higher. Diffusion through palladium takes places considerably below 200°C. Molecular hydrogen diffuses through nickel at about 450°C, and through copper at about 640°C and higher. Commercial copper, reduced with hydrogen at around 600°C, becomes brittle, but not pure copper. The reason for this is that commercial copper contains Cu_2O.[10] Chromium does not adsorb hydrogen, and the increase of the stability of platinum and steels containing chromium is due to this property as it lowers the adsorbing power of these metals when alloyed with them.[11]

The ionization potential of hydrogen is 17.9 volts. This is the approximate magnitude of the ionization potentials of the metals forming typical hydrogenation catalysts ($Cr = 16.6$; $Fe = 16.5$; $Ni = 18.2$; $Cu = 18.2$; $Pd = 19.8$?). The ionization reaction is as follows:

$$H_2 \rightarrow \underset{\text{labile}}{H_2^+} + \bar{e} \rightarrow H^+H + \bar{e}17.9 \text{ volts}$$

In thermal homogeneous dissociation atoms and not ions are formed: $H_2 \rightarrow 2H$.[12]

Nascent hydrogen, at room temperature, diffuses through palladium, platinum, and iron; it diffuses very slowly through nickel, but it does not diffuse through copper.[13]

Much has been written about the possibility that hydrogen forms definite hydrides with the metals acting as catalysts in hydrogenation, and most likely the condition is that the metal-like hydrides are not true compounds, but that the metals can take up various amounts of hydrogen by the combined forces of diffusion, solubility and adsorption until saturation is achieved. This amount will, at least in certain cases, depend on the physical condition of the metal. The binding of the hydrogen, in most cases, is likely to be considered as physical, since the hydrogen does not change the lattice structure or the property of the metal, except in cases, where the affinity is strong, e.g., for nickel, palladium and platinum. A minimum of hydrogen is taken up by Cr, Mo, W and U. The gaseous hydrides are definite chemical compounds, and many of them are prominent catalyst poisons, probably owing to their high reactivity. It is possible that many of these hydrides would be found to be promoters in concentrations lower than those in which they act as poisons, a matter which requires future study. The salt-like hydrides are typical polar compounds in which the hydrogen is of electronegative character. The following table by Pietsch gives a good classification of the various hydrides:[14]

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[10] Sieverts: *Z. phys. Chem.*, **60**, 196 (1907).

[11] Adadurov et al.: *Kharkov Khim.-Teknol. Inst. S. M. Kirova.*, **1**, 12 (1939).

[12] Schmidt: *Z. Elektrochem.*, **39**, 824, 969 (1933).

[13] *Gmelins Handbuch der anorganischen Chemie:* Wasserstoff.

Salt-like hydrides		Metal-like hydrides		Gaseous hydrides	
He	Li Be B	Al		C	N O F
Ne	Na Mg	Sc	Ti V Cr Mn Fe Co Ni Cu Zn Ga	Si	P S Cl
Ar	K Ca	Y	Zr Nb Mo Ma Ru Rh Pd Ag Cd In	Ge	As Se Br
Kr	Rb Sr	*	Hf Ta W Re Os Ir Pt Au Hg Tl	Sn	Sb Te I
Xe	Cs Ba	Ac	Th Pa U	Pb	Bi Po —
Em	— Ra				

The technical production of hydrogen is of enormous importance in many catalytic manufacturing processes, but only a very brief description can be given here because the manufacture of hydrogen is not necessarily combined with catalytic reactions (e.g., electrolysis).

Metals react with water, under various conditions, to produce hydrogen, the most frequently used metal being iron. Using finely divided iron powder, as obtained by reduction of organic iron compounds, the iron reacts with water at ordinary temperature.[15] In the earliest days of this process, filings and shavings were used, but now, iron ore is utilized.

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[14] Pietsch: *Z. Elektrochem.*, **39**, **577** (1933).

[15] Job and Reich: *Compt. rend.*, **177**, 1439 (1857).

* Rarer earths

The reaction mechanism is as follows:

$$\begin{array}{ll} 1. & 3Fe + 3H_2O \rightleftarrows 3FeO + 3H_2 \\ \underline{2.} & \underline{3FeO + H_2O \rightleftarrows Fe_3O_4 + H_2} \\ 3. & 3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2 \end{array}$$

It is noted that the process from right to left is a reduction. In practice, this step is effected by water gas:

$$\begin{array}{ll} 1. & Fe_3O_4 + CO \rightleftarrows 3FeO + CO_2 \\ 2. & 3FeO + 3CO \rightleftarrows 3Fe + 3CO_2 \end{array}$$

In industrial practice, temperatures from 550 to 800°C are used.

It is thought that the reduction of the oxide may be due to hydrogen formed intermediately:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Two types of generators are used: (1) several small iron retorts externally heated; or (2) one large single retort internally heated.[13]

Bergius [16] produces very pure hydrogen, using iron scrap and water at 300 to 350°C and about 500 atmospheres pressure. Under these conditions, the water is highly reactive so that the iron goes into solution in much the same way it would in a solution of a substantially strong acid under liberation of hydrogen. Due to hydrolysis, iron oxide is precipitated. This process is catalyzed by ferrous salts, copper, and noble metals (in catalytic form). The process proceeds quantitatively. The iron oxide obtained is very fine and is readily reduced again. The hydrogen obtained is very pure (99.9%). Where the hydrogen is required at high pressure, it can be taken directly from the generator, when this process is used.

Hydrogen may also be made from water gas which is formed by the action of steam on incandescent coke around 1400°C.

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[16] Bergius: *J. Soc. Chem. Ind.*, **32**, 462 (1913); German Patents, 254,593 (1911) and 277,501 (1913).

Below 1000°C, carbon dioxide is formed, until below 400°C the carbon is converted almost exclusively into carbon dioxide. The reaction mechanism above 1000°C is as follows:

1. $2H_2O \rightarrow 2H_2 + O_2$ —115,600 calories
2. $2C + O_2 \rightarrow 2CO$ +58,400 calories

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3. $2C + 2H_2O \rightarrow 2CO + 2H_2$ —57,200 calories

Below 400°C, the conversion takes place according to:

$$C + 2H_2O \rightarrow CO_2 + 2H_2 - 18{,}000 \text{ calories}$$

The CO is removed by catalytic oxidation to CO_2 or by liquefaction. In the catalytic oxidation, water is brought to react with the CO:[17, 18]

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The steam is passed over an iron catalyst, and by using an excess of steam and by absorbing the CO_2 in water at a pressure of 25 to 30 atmospheres, the process is forced to the right. The equilibrium constant is calculated from [17]

$$k = \frac{[CO][H_2O]}{[CO_2][H_2]}$$

Temperature, °C:	786	886	1086
Value of k:	0.81	1.19	1.95

Iron oxide, alone or in combination with other metals (Cr, Sb, Ag, Cu, Ni, etc.), is a suitable catalyst.[19, 20]

Hydrogen may also be manufactured from hydrocarbons, especially from methane, by pyrolysis (around 1100 to 1200°C),[21] or by reacting the hydrocarbon with steam.[22, 23, 24, 25] The reaction, in the presence of steam, is as follows:

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[17] Hahn: *Zeit. phys. Chem.*, **42**, 705 (1903); *ibid.*, **44**, 513 (1903); *ibid.*, **48**, 735 (1904).

[18] Naumann and Pistor: *Ber.*, **18**, 2724, 2894 (1885).

[19] Bosch: *Chem. Ztg.*, **44**, 721 (1920).

[20] Taylor, H. S.: *Industrial Hydrogen*, Am. Chem. Soc. Monograph, New York, Reinhold Publishing Corp., 1921.

[21] Hurd, C. D.: *The Pyrolysis of Hydrocarbons*, A. C. S. Monograph, New York, Reinhold Publishing Corp., 1929, p. 50.

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$

This reaction starts above 350°C, the conversion rate increasing fast between 500 and 800°C, full conversion being arrived at around 1000°C. The process is quantitative at around 1300°C. By using excess of steam, the conversion proceeds at lower temperatures, and carbon deposition is prevented. This is especially important when higher hydrocarbons are present as they tend to deposit carbon on the catalyst. Nickel or cobalt, promoted with alumina or thoria and supported on fire clay, magnesium oxide, or brick gives good conversion below 1000°C.[23] Other catalysts are Pt, Pd, Ag, and Cu,[26] Ni on magnesia,[27] etc. If a larger proportion of steam is used and the temperature is lowered, the following reaction takes place:

$$CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$$

Almost complete conversion of methane by steam is obtained between 400 and 600°C.[28] The CO_2 can be removed by means of oxides which are regenerated by calcination, or by absorption in water under pressure. Suitable catalysts are iron promoted with alumina and KOH at 500°C, nickel on refractory oxides, nickel or copper on alumina,[29] etc.

Methane (natural gas) and CO_2 react as follows:

$$CH_4 + 3CO_2 \rightleftarrows 4CO + 2H_2O$$

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[22] Fischer and Tropsch: *Ibid.*, **9**, 39 (1928).

[23] Marek, L. T. I. and D. A. Hahn: *The Catalytic Oxidation of Organic Compounds in the Vapor State*, Am. Chem. Soc. Monograph, New York, Reinhold Publishing Corp., 1932.

[24] Neumann and Jacob: *Z. Elektrochem.*, **30**, 557 (1927).

[25] Sabatier and Senderens: *Compt. rend.*, **134**, 514 (1902).

[26] Bone and Andrew: *Proc. Chem. Soc.*, **22**, 78 (1906).

[27] German Patent, 296,866 (1912).

[28] British Patent, 291,244 (1928).

[29] Fraser: *Trans. Elektrochem. Soc.*, **71**, 1 (1937) (Reprint).

at 900 to 1100°C and over a nickel catalyst, the CO being oxidized to CO_2 as indicated above.[30] Gases, from hydrogenation of coal, are also treated with steam to form CO and hydrogen, the CO being oxidized catalytically to CO_2.[30a]

A great many patents have been taken out on production of hydrogen from water gas, natural gas, and other sources, but to review even a few of these processes would be outside the scope of this book.

Group I: Li (6, 7), Na, K (39, 41), Rb (85, 87), Cs (alkalis and alkaline earths, Cl_2, I_2, F, SO_4, CO_3, NO_3, SiO_2, Fe, traces of heavy metals).*
Cu (63, 65) (Ag, Al, As, Bi, Cd, Co, Fe, Mn, Ni, P, Pb, Sb, Sn, Zn).
Ag (107 109) (Cd, Cu, Fe).
Au (Ag, Cu, Fe, Na, Pb, Pt metals, Sn, Zn).

Of the alkalies,** sodium is used as a polymerization catalyst in making synthetic Buna rubbers. Lithium is used in the form of its salts in the preparation of ketones,[31, 32] and also instead of magnesium in the Grignard reaction.[33, 34, 35, 36]

Metallic copper is used in the dehydrogenation of aldehydes and ketones, alone or in combination with other elements such as in a chromite.[37, 38, 39] Backhaus precipitates copper hydroxide with ammonia on a copper wire in a copper tube and reduces with hydrogen at 300°C; this catalyst is used for dehydrogenating alcohols to aldehydes. Metallic copper is also used as an oxidation catalyst in the form of wire, gauze, or foil the surface of which is treated with acetic acid in an oxygen atmosphere and reduced with hydrogen.[38, 39] Copper, reduced from the oxide and containing 0.1 per cent of nickel, easily hydrogenates benzene at 225°C under atmospheric pressure.[40]

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[30] German Patent 306,301 (1914).

[30a] German Patent, 435,588 (1924).

[31] Kroenig: *Z. angew. Chem.*, **37**, 667 (1924).

[32] Rojahn and Schulten: *Ber.*, **59**, 499 (1926).

[33] Gilman and Young: *J. Am. Chem. Soc.*, **56**, 1415 (1934).

[34] Osborg, H.: *Lithium, Theoretical Studies and Practical Applications*, New York, The Electrochemical Society, 1935.

[35] Schoenberg et al.: *Ber.*, **64**, 2322, 2577 (1931); *ibid.*, **66**, 237, 245 (1933).

[36] Ziegler et al.: **479**, 135 (1931); *Ber.*, **63**, 1847 (1930).

[37] Williams, E. C. and M. de Simo: *Dehydrogenation of Oxyorgano Compounds*, Twelfth Report of the Committee of Catalysis, National Research Council, New York, John Wiley & Sons, 1940.

[38] Backhaus: U. S. Patent, 1,375,345 (1931).

[39] Backhaus and Arentz: U. S. Patent 1,376,655 (1931).

* The numbers in parentheses indicate the various isotopes (see Ashton page 123). The elements and compounds in the parentheses are impurities which are listed in literature as having been found in the substance or substances in question.

** The alkalies and alkaline earths form readily removable constituents in alloys which can be used for making catalysts.

The reduction of CuO, with hydrogen, proceeds slowly at 150°C, but rapidly at 200°C. The reduced copper acts as an activator for the hydrogen, thus increasing the velocity of the reduction on the interface Cu/CuO autocatalytically.[41, 41a, 42, 43, 44] Copper catalysts may also be made from alloys from which one of the components is dissolved out leaving a porous catalyst.[45] Bladger and Clark[46] suggest the use of alloys containing magnesium: Cu-Mg:85-15%; Cu-Fe-Mg: 75-10-15%; Cu-Ni-Mg:40-40-20%. Barker[47] prepared copper alloys with iron and manganese and treated the surface with acids to form metallic salts, or oxidized the surface of the alloy and reduced the oxide layer so as to leave a spongy metallic surface.

Hara[48] made three types of copper catalysts:

Catalyst	Catalytic properties
1. Copper hydroxide prepared by precipitation of copper sulfate with an equivalent amount of sodium hydroxide, drying at 100°C and reduction at 250°C. Contains a small amount of basic copper sulfate	Especially suitable for dehydrogenation of secondary alcohols with formation of unsaturated hydrocarbons

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[40] Ipatieff: *Bull. soc. chim.*, **7**, 281 (1940); *Chem. Abstracts*, **36**, 4014 (1942).

[41] Jones and Taylor: *J. Phys. Chem.*, **27**, 623 (1923).

[41a] Canadian Patent, 384,172 (1939).

[42] Lange: U. S. Patent, 2,237,353 (1941).

[43] Pease and Taylor: *J. Am. Chem. Soc.*, **43**, 2179 (1921).

[44] Sabatier: *Compt. rend.*, **125**, 101 (1897).

[45] I. G. Farbenindustrie, A.-G.: British Patent, 282,112 (1927).

[46] Bladger and Clark: French Patent, 672,626 (1930).

[47] Barker: U. S. Patents, 1,936,563, 1,936,564, and 1,936,565 (1933).

[48] Hara: *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, **A 9**, 405 (1926); Bruckner: Katalytischie Reaktionen, etc.; Steinkopff, Dresden, 1930.

Catalyst	Catalytic properties
2. As (1), but precipitated with an excess of sodium hydroxide	Dehydrogenation of secondary alcohols to aldehydes and ketones
3. Calcination of copper nitrate, and reduction of the oxide at 220°C	Suitable for both preceding conversions, especially for conversion of the alcohols of the cyclohexane series to the corresponding ketones

By precipitating the nitrate of copper, nickel, or silver with a rare earth, e.g., samarium, a mixed oxide, consisting of 95.0 to 99.75 per cent of the oxides of copper, nickel or silver and 5.0 to 0.25 per cent of rare earth oxide, is produced. This catalyst is used for the partial oxidation, in the vapor phase, of organic compounds such as low-molecular monovalent alcohols into aldehydes, ketones and acids; ethylene to formaldehyde; toluene to benzaldehyde and benzoic acid.[49]

Copper-chromium oxide has been studied extensively by Adkins [50] and by Lazier.[51] According to Adkins et al.[50, 52] this catalyst can be prepared by: (1) the decomposition of precipitated copper ammonium chromium carbonates; (2) the decomposition of copper ammonium chromate; (3) the decomposition of copper-chromium nitrates; (4) the grinding or heating together of copper and chromium oxides. Adkins suggests that probably the real catalyst is copper oxide stabilized toward reduction by chromium oxide and that a good catalyst is likely to be obtained by any method that produces cupric oxide in combination with a stablizing substance such as chromium oxide. The chromite catalyst, prepared by Adkins, contains divalent copper.

Schmidt [53] hydrogenated fats at high pressure in vapor phase at 300°C to produce hydrocarbons and alcohols using a copper contact.

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[49] Day: U. S. Patent, 1,871,117 (1932); *J. Phys. Chem.*, **35**, 3272 (1931).

[50] Adkins, H.: *Reactions of Hydrogen with Organic Compounds over Chromium Oxide and Nickel Catalysts*, Madison, The University of Wisconsin Press, 1937, p. 12.

[51] Lazier: British Patent, 301,806, (1926); U. S. Pat., 1,746,783, (1930).

[52] Adkins, Connor and Folkers: *J. Am. Chem. Soc.*, **54**, 1138 (1932).

[53] Schmidt: *Ber.*, **64B**, 2051 (1931).

In the reduction of carbon monoxide at elevated temperature, the hot parts of the apparatus are coated or lined with copper, silver, aluminum or their alloys, whereas metals of lower melting point or non-metallic materials are used for the less hot parts.[54]

Frolich et al.[54a] prepared copper-zinc catalysts, containing 95 per cent copper oxide and 5 per cent zinc oxide, by various procedures. The relative activities of the resulting catalysts, in the decomposition of methyl alcohol at 360°C and a total pressure of one atmosphere, were as follows:

Hydroxides precipitated together	100
Hydroxide gels mixed	83
Zinc precipitated on suspended copper hydroxide	75
Calcined mixed nitrates	70
Copper precipitated on suspended zinc hydroxide	67

Copper catalysts may also conveniently be made from organic salts which are readily decomposed such as the formate, acetate, or oxalate.

Silver oxide, Ag_2O, is a mild oxidation catalyst very suitable for vapor-phase reactions. The oxidizing action of the silver oxide is enhanced by the presence of samarium oxide.[49, 55] The silver oxide, Ag_2O, decomposes a little above 300°C, the reaction being: $2Ag_2O \rightarrow 4Ag + O_2$. It is reduced by hydrogen at 100°C or less, and in the presence of a trace of moisture. The reduction proceeds at room temperature.[56, 57] A highly active metallic silver catalyst is prepared by catalytic reduction of an aqueous solution of a silver compound, e.g., $AgNO_3$, by nascent hydrogen generated in the aqueous medium. Silver lends itself to production of colloidal solutions of the metal mixed with its oxides, and it is reasonable to assume that such colloids will be of substantial interest in catalytic reactions.

Colloidal gold solutions have been widely studied by Zsigmondy et al.[58, 59] They are active in the decomposition of hydrogen peroxide, and especially so when the sols are alkaline; neutral gold sols are only slightly or not at all active.[58] It is considered important that the gold sol is fully reduced and free from oxide. According to Thiessen,[60] the unreduced gold compounds are readily detected by testing with pure ammonia. The red gold sols, described by Zsigmondy, do not react with ammonia and are considered pure.

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[54] Johnson (I. G. Farbenindustrie): British Patent, 231,285 (1925).

[54a] Frolich, Fenske and Quiggle: *Ind. Eng. Chem.*, **20**, 694 (1928).

[55] Addicks, L.: *Silver in Industry*, ACS Monograph, New York, Reinhold Publishing Corp., 1940.

[56] Colson: *Compt. rend.*, **130**, 330 (1900); *ibid.*, **132**, 467 (1901).

[57] Kohlschütter: *Z. Elektrochem.*, **14**, 49 (1908).

The relationship between the degree of dispersion of gold sols and their power in decomposing hydrogen peroxide was studied by Rusznyak,[61] the time for decomposing half of the hydrogen peroxide in each sol being taken as a measure for the catalytic activity. The concentration was 0.000,022 gram-atom gold per liter. It was found that the sols of lowest degree of dispersion were those of highest activity.

Sol. No.	Color	Particle size, μμ	Time of 50% decomposition, Minutes
I	blue	42–42	13.9
II	violet	31–32	29.2
III	red	29–29	32.0

Group II: Be, Mg (24, 25, 26), Ca (40, 44), Sr (86, 87, 88), Ba (135, 136, 137, 138), Ra (alkalies and alkaline earths, Fe, SiO_2, Cl, SO_4, NO_3, NH_3, traces of heavy metals).*
Zn (64, 66, 67, 68, 70) (Ag, As, Bi, C, Ca, Cd, Cu, Fe, In, Mg, Pb, S, Sb, Si).
Cd (110, 111, 112, 113, 114, 116) (Bi, C, Cu, Fe, Ni, Pb, Sn, Th, Zn).
Hg (196, 197, 198, 199, 200, 201, 202, 203, 204) (Fe, traces of heavy metals).

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[58] Zsigmondy, R. and A. Thiessen: *Das kolloidale Gold*, Leipzig, Akademische Verlagsgesellschaft, 1925.

[59] Zsigmondy, R.: *Kolloidchemie*, Leipzig, Verlag Otto Spamer, 1925.

[60] Thiessen: *Zeit. anorg. & allgem. Chem.*, **134**, 357 (1924).

[61] Rusznyák: *Z. phys. Chem.*, **85**, 681 (1913).

* The numbers in parentheses indicate the various isotopes (see Ashton page 123). The elements and compounds in the parentheses are impurities which are listed in literature as having been found in the substance or substances in question.

The use of zinc chloride (oxychloride, NO_3, SO_4, NH_3, Fe, Pb, heavy metals) in Friedel and Crafts reaction and in halogenations is well known. Zinc oxide (Fe, Pb, Zn, Cl, SO_4, As_2O_3, CO_3) is used as a catalyst in the hydrolysis of fats, in alkylation of amines, dehydration of alcohols, hydrogenation and dehydrogenation, hydrolysis and hydrations, polymerizations, etc. The characteristics of the surface of the zinc oxide substantially determine its activity as a catalyst.[62, 63] Thus, it has been found that the activity of the zinc oxide is directly proportional to the surface area.[63]

Steacie and Elkin[64] studied the decomposition of methanol using solid and liquid zinc as catalyst, the zinc being purified and vacuum-distilled and finally reduced with hydrogen in situ in order to avoid contamination with zinc oxide. The temperature range investigated was from 360 to 440°C. The catalytic activity increased with the rise of temperature, but there was no discontinuance of activity at 420°C, i.e., the melting point of the zinc. The interpretation of this experiment was that the catalytic activity of a solid substance cannot generally be said to be the function of limited parts of the surface.

Frolich, Davidson, and Fenske[65] studied the properties of methanol catalysts composed of copper and zinc, prepared by precipitating the mixed hydrates from their nitrate solutions, dehydrating the gel, and then reducing the oxides with methanol vapor at the lowest temperature at which reduction of the copper oxide takes place, i.e., 200–220°C. The ZnO was partly reduced under these conditions. X-rays showed that the copper has the same structure as the metal in bulk, and the oxide as that prepared by any other method. The unit-cell sizes of both are markedly influenced by the presence of the other constituent, the side of the unit cell of the copper lattice expands with increasing additions of ZnO, then passes through a maximum between 50–60 mol per cent ZnO, decreases somewhat, and then rises again. The

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[62] Hüttig and Fehér: *Z. anorg. allgem. Chem.*, **197**, 129 (1931).

[63] Siller: *J. Am. Chem. Soc.*, **65**, 431 (1943).

[64] Steacie and Elkin: *Proc. Roy. Soc., London*, **A 142**, 457 (1933); *J. Am. Chem. Soc.*, **58**, 691 (1936).

[65] Frolich, Davidson and Fenske: *Ind. Eng. Chem.*, **21**, 109 (1929).

maximum elongation recorded is 1.3 per cent, corresponding to 90 mol per cent ZnO, which is the highest concentration studied. The unit cell of ZnO suffers similar elongation on addition of copper, with the exception that the curve first passes through a minimum value for admixture of 10–20 per cent of copper.

Zinc is also used as an auxiliary drier in paints and varnishes together with cobalt, and it is said that it counteracts the fast surface drying of the cobalt and thus prevents wrinkling.[66, 67]

Cadmium has not found much application as a catalyst. Reppe and Wolff [68] used it as an alternative to zinc in the form of a salt of an organic acid on a carrier of active charcoal or pumice for condensing acetylene with phenols. It is also claimed that cadmium or mercury vapors act as polymerization catalysts for conversion of gaseous hydrocarbons to higher liquid ones when the metal vapors are led over graphite or coke catalysts heated to high temperature.[69] Cadmium metaphosphate, made by heating $Cd(H_2PO_4)_2$ to 250–350°C, is suggested as a catalyst for production of acetaldehyde from acetylene and steam.[70]

Mercury is used as an oxidation catalyst in strong sulfuric acid in Kjeldahl analyses, and mercury salts are used for hydration of acetylene to acetaldehyde (see page 326). When passing CCl_2F_2 and F over a mercury catalyst at 340 to 370°C, a quantitative yield of $CClF_3$ is obtained.[71] Mercury is also used for preparing base metal catalysts from amalgams by distilling off the mercury.[72]

Group III: B (10, 11), Al (Ca, Cu, Mg, Mn, Ti, Zn), Ga, In (As,
Cu, Ga, Pb, Zn, Tl).*
Sc, Y, Rare Earths, Ac.

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[66] Metasap Chemical Co., Harrison, New Jersey: *Metallic Soaps*, 1940.

[67] *Technical Manual of the Use of Driers for Paint and Varnish Chemists*, Elizabeth, N. J., Nuodex Products Co., Inc., 1940.

[68] Reppe and Wolff: U. S. Patent 2,017,355, 1935.

[69] German Patent, 626,338 (1935).

[70] Groombridge and Dee: U. S. Patent 2,206,226 (1940).

[71] Simonds, Bond and McArthur: *J. Am. Chem. Soc.*, **62**, 3477 (1940).

[72] Bennet and Fraser: U. S. Patent, 1,893,879 (1933).

* The numbers in parentheses indicate the various isotopes (see Ashton page 123). The elements and compounds in the parentheses are impurities which are listed in literature as having been found in the substance or substances in question.

Boron halides, especially the fluoride, are finding wide interest as catalysts for a number of organic reactions such as alkylation, polymerization, condensation, etc. Boric acid (Fe, Ca, As_2O_3, SO_4, Cl, traces of heavy metals) is an effective polymerization catalyst.[73]

Alumina, Al_2O_3 (Cu, Fe, Ga, Mn, Sn, Zn, SO_4, Cl, H_2O, SiO_2, alkalies and alkaline earths) is used, to a considerable extent, as a catalyst and also as a catalytic support. Active alumina to be used for catalytic purposes must be soluble in hot mineral acids and convertible into aluminate in a concentrated solution of sodium hydroxide. To meet these specifications, the alumina must not be overheated during the preparation. Precipitated alumina, for catalytic use, should not be heated above 400°C.[74] If it is heated at red heat, its catalytic properties for the dehydrogenation of alcohols are destroyed.[75]

According to Groll and Roberts,[76] the particular form of activated alumina which has been found satisfactory as a catalyst for dehydrogenation is the commercial product which is sold as a drying agent. This alumina, which is made by calcining a specially crystallized trihydrate of aluminum, has a very porous structure. The authors prepared an activated alumina in the laboratory, which compared well with the commercial product, by precipitating aluminum hydroxide, obtained by dissolving aluminum in sodium hydroxide, from the solution by means of carbon dioxide gas, carefully washing the resulting precipitate, and drying at 600°C. This catalyst worked well for dehydrogenation of hydrocarbons when there was 0.1 mol per cent of water in the hydrocarbon feed. (In this connection cf. Boswell and Dilworth.[77])

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[73] Burk, R. E.: *Catalysis in Polymerization*, Twelfth Report of the Committee on Catalysis, National Research Council, New York, John Wiley & Sons, Inc., 1940, p. 180.

[74] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures*, New York, The Macmillan Co., 1937.

[75] Sabatier, P. and E. Emmett Reid: *Catalysis in Organic Chemistry*, New York, D. Van Nostrand Co., 1923.

[76] Groll and Roberts: *Refiner Natural Gasoline Mfr.*, Oct., 1938 (Reprint).

[77] Boswell and Dilworth: *Bull. #6, School of Engineering Research, University of Toronto*, 1926.

The authors also used activated alumina as a carrier for different dehydrogenation catalysts and found that the chrome-alumina catalyst gave the best results.[76] This catalyst was prepared by impregnating activated alumina with an aqueous solution of chromic acid or one of its salts, such as sodium or potassium chromate or bichromate. Catalysts, prepared with alkali chromium salts, give most satisfactory conversions, with concentrations of about 2 per cent chromium; if the salt content is increased beyond the optimum figure, the activity of the catalyst decreases owing to the increasing formation of an alkali aluminate.

The presence of alkali may be avoided by the use of chromic acid or chromium nitrate in the preparation of the catalyst. In this manner, on raising the chromium concentration to 10 or 20 per cent, a catalyst is obtained which is active at temperatures 50 to 70°C lower than activated alumina, containing little or no chromium oxide.

Experiments showed that the catalytic activity of activated alumina closely parallels its adsorptive capacity, the decrease in adsorptive capacity and activity for five catalysts decreasing as follows:

> Chromic acid-alumina (15.1% Cr) > Chromic acid-alumina (1.9% Cr) > Activated alumina > Sodium bichromate-alumina (7.5% Cr) > Sodium bichromate-alumina (15.0% Cr).

The presence of the alkali, which is detrimental to the activity of the catalyst, is also detrimental to the adsorptive capacity.

The activity of these catalysts declines as a result of accumulation of carbon upon the surface and in the pores of the catalyst during the dehydrogenation process. To restore the original activity of the catalyst, this carbon deposit must be periodically removed. The removal is best accomplished by treating the catalyst at a temperature of 600 to 700°C with a stream of air. The heat of combustion is sufficient to cause a sharp rise in the temperature of the catalyst bed, and the air flow must be carefully controlled in order to keep the temperature within safe limits at about 700°C. The time, necessary for regeneration, can be reduced to one half or one third (without at the same time permitting excessive temperatures) by diluting the air with an inert gas such as nitrogen or carbon dioxide or, in some cases, steam; these diluents serve to increase the rate of removal of the heat generated in the tube.

In actual practice, the course of the regeneration may be followed by the course of the combustion zone which progresses from the inlet end of the tube to the exit end, a sharp decline in temperature and decrease in the carbon dioxide content of the effluent gas occurring when the combustion zone reaches the exit end. The catalyst is now ready for reuse. Both plain activated alumina and the chrome-alumina catalysts have been regenerated in this manner over 200 times with very little loss in activity.

Lepsoe and Mills[78] have developed a porous catalyst containing aluminum trihydrate in which at least part of the water of hydration is retained, this catalyst being used in the reduction of sulfur dioxide in flue gases to elemental sulfur. The preferred preparation of this catalyst is as follows:

"One part by volume of fire clay, one part aluminum trihydrate, and two parts of sawdust are intimately mixed together, adding 1.75 parts of aqueous sodium silicate having a specific gravity of approximately 1.27. This material, which is plastic, is molded into bricks of suitable size, and is dried slowly in a furnace, finally being subjected to sufficiently high temperature to cause sintering of the mixture and fusing of the aluminum hydrate with the aid of the sodium silicate, at the same time burning out the sawdust so as to render the bricks porous. The water of hydration is retained at least in part by regulating the temperature of the furnace during the drying and sintering of the bricks so that it shall not exceed 593°C, the desirable temperature for the sintering being between 538 and 593°C."

Aluminum halides are used as polymerization catalysts, the chloride and bromide also serving as catalysts for alkylation, isomerization, cracking, hydrogenation and dehydrogenation. The properties and uses of aluminum chloride (Fe, SO_4, traces of heavy metals) have been thoroughly discussed by Thomas et al.[79] The iron content of this compound should be low.

Cerium oxide is an active oxidation catalyst, and is used as such in oxidation of ammonia and carbon monoxide. Cerium salts are effective oxidation catalysts in solutions. Cerium has been used as a catalyst for hydrogenation of the ketone from stearic acid.[80] Cerium oxides may also be used in dehydrogenation.[81]

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[78] Lepsoe and Mills: U. S. Patent 2,080,359 (1937).

[79] Thomas, C. H., M. B. Moshier, K. E. Morris and R. W. Moshier: *Anhydrous Aluminum Chloride in Organic Chemistry*, New York, Reinhold Publishing Corp., 1941.

[80] Kino and Kato: *J. Soc. Chem. Ind., Japan*, **42**, Suppl. Bindings 362 and 363 (1939); *Chem. Abstracts*, **34**, 2237 (1940).

[81] Briggs and Taylor: *J. Am. Chem. Soc.*, **63**, 2500 (1941).

Group IV: C (12, 13), Si (28, 29, 30), Ge (70, 72, 73, 74, 76), Sn (112, 114, 116, 117, 118, 119, 120, 121, 122, 124) (Ag, Al, As, Bi, Cd, Cu, Fe, Pb, Sb, Zn), Pb (203, 204, 205, 206, 207, 208, 209, 210) (Ag, As, Bi, Cd, Cu, Fe, Hg, Mg, Ni, Sb, Sn, Te, Tl, Zn).*
Ti, Zr (90, 92, 94, 96), Hf, Th.

Carbon in its activated form is a good catalyst. Hilditch and Hall [13] describe a process in which wood or another material is first heated in retorts at 400 to 500°C until all of the volatile products are driven off. Then, the temperature is raised to 800 to 1,000°C, when a current of steam, air or carbon dioxide is passed through the carbonized mass. Whereas these agents are the usual activators, other activating substances, such as chlorine, phosphorus, gaseous hydrochloric acid, and sulfur, may also be used. The function of this oxidation is to remove the surface film of complex hydrocarbons formed on the carbon particles, and by partial oxidation of the carbon, to leave an unsaturated lattice structure of carbon atoms on the surface. The hot product is discharged into water, lixiviated with hot water, then with hot mineral acid, and finally again with hot water, when the carbon is dried and granulated or ground to suit specifications. Other processes for preparing active carbons have been reported by Brauer and Reitstötter.[82] Catalytically active carbon serves as a catalyst in the manufacture of phosgene, hydrochloric and hydrobromic acids, sulfuryl chloride, in processes of polymerization, oxidation, alkylation, hydrogenation of halogen derivatives, in making acetyl chloride, etc. According to Hilditch and Hall, very active hydrogenation catalysts are made by depositing copper, nickel, palladium or platinum on active carbon.[13]

The properties of carbon blacks were studied by Smith, Thornhill and Bray,[83] the surface areas of different blacks in square meters per gram being:

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[82] Brauer and Reitstötter: *Z. angew. Chem.*, **41**, 536 (1928).

[83] Smith, Thornhill and Bray: *Ind. Eng. Chem.*, **33**, 1303 (1941).

* The numbers in parentheses indicate the various isotopes (see Ashton page 123). The elements and compounds in the parentheses are impurities which are listed in literature as having been found in the substance or substances in question.

Thermal decomposition and other non-impingement blacks	15–64
Channel blacks	around 100
Ink and color blacks	100–1000

Silica gel, SiO_2, is made from sodium silicate, hydrogen silicide or silicon tetrafluoride or tetrachloride. In the case of sodium silicates, acid precipitation and subsequent washing is used, and for the silicide and the fluorides, the conversion is achieved by hydrolysis. The most important, but also most difficult, operation, in preparing silica gels of high activity, is the drying. For high absorbing power, drying between 100 and 120°C is adequate, but for making merely a support material, temperatures between 200 and 300°C may be used. For making highly active silica gels, the moisture may also be replaced by a solvent, e.g., ethyl alcohol, which, in turn, is expelled by the action of infra-red radiation (Lohse). When ordinary drying is used, the gel is dried to a water content of 5–8 per cent or lower, and the lower the moisture content is, for the same pore volume, the more effective is the gel. The surface of the gel is about 450 square meter per gram, the pore volume being 40 to 45 per cent of the total volume.[84, 85] Silica is an active catalyst for the oxidation of nitric oxide by oxygen,[75] for decomposition reactions, etc.

Tin compounds, such as tin sulfide, tin oxalate, or tin oxide are used as catalysts in hydrogenation cracking of coal, tars and oils. $SnCl_4$ activates $AlCl_3$ in Friedel-Crafts reactions and acts as a polymerization catalyst for styrene.[86] Complex tin compounds act as catalysts in polymerization of 1,3-butadienes.[87] Tin itself is a catalyst for esterification of oils with glycerol.[88] A highly active tin contact is claimed to be made by precipitating $SnCl_2$ with Na_2CO_3, oxidizing and then reducing at 235–300°C.[89]

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[84] Bruckner, H.: *Katalytische Reaktion in der organisch-chemischen Industrie, I. Teil,* Dresden, Verlag Theodor Steinkopff, 1930.

[85] Ruff and Mautner: *Z. angew. Chem.,* **40**, 428 (1927).

[86] Williams: *J. Chem. Soc.,* **246**, 1046 (1938).

[87] I. G. Farbenindustrie, A.-G.: French Patent, 847,876 (1939); *Chem. Abstracts,* 35, 5602 (1941).

[88] Kawai and Zamomoto: *J. Soc. Chem. Ind., Japan,* **43**, Suppl. Binding 219 (1940); *Chem. Abstracts,* 35, 1255 (1941).

[89] Brown and Henke: *J. Phys. Chem.,* **27**, 739 (1923).

Lead is used as a catalyst in reduction of nitrobenzene to aniline.[90, 91] This catalyst is made by calcining lead carbonate (Cl, SO_4, Al_2O_3, CaO, Fe, traces of heavy metals) or lead nitrate (Cl, Cu) at 430°C when Pb_3O_4 is formed. This, in turn, is converted to PbO at 600°C and reduced at 350°C. Lead sulfide (Cl, Cu, Fe) is used as a catalyst in the polymerization of olefines.

Zirconia, ZrO_2 (Natural: Al, Bi, Ca, Cu, Dy, Fe, Mg, Mn, Si, Sn, Th, Ti, U) is a very good catalytic agent, used alone or as an admixture to other catalysts. It may replace fused alumina or thoria, as a catalyst, in preparing HCN from formamide.[92] Other uses are as a catalyst in vapor phase esterification, decomposition, dehydration, dehydrogenation, etc.

Titania, TiO_2(Cl, SO_4, Ca), is used as an esterification catalyst in vapor-phase reactions between 280 and 300°C, esters of a primary alcohol and an aliphatic acid, except formic acid, being formed.[75] This oxide is also a catalyst in the formation of HCN from carbon monoxide and ammonia.[93, 93a] Atack [94] used titania as a catalyst for the oxidation of anthracene to anthraquinone, and of naphthalene to phthalic acid. The various methods for preparation of active titania catalysts have been discussed by Rudisill and Engelder.[95] The hydroxide precipitated from titanium oxysulfate with ammonia or made by hydrolysis of dilute solutions of titanium chloride, the acids being removed by washing, gave best results in decomposing alcohol to ethylene at 350°C.

Group V: N (14, 15), P, As, Sb (121, 123), Bi.
V, Cb, Ta, Pa.

Phosphoric acid, H_3PO_4 (Cl, NO_3, SO_4, alkalies, Ca, Mg, As_2O_3, Fe, O_2, Pb), has a considerable importance as a catalyst in alkylation, polymerization and hydration of olefines, and

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[90] Grills and Brown: *J. Phys. Chem.*, **45**, 234 (1941).

[91] Madenwald, Henke and Brown: *J. Phys. Chem.*, **31**, 862 (1927).

[92] Evan and Imperial Chemical Ind., Ltd.: British Patent, 305,816 (1929).

[93] Swiss Patent 111,726 (1926); Berkman, Morrell and Egloff: *Catalysis, Inorganic and Organic*, New York, Reinhold Publishing Corp., 1940.

[93a] Ipatieff: U. S. Patent 2,018,065 (1935).

[94] Atack: British Patent 182,843 (1922).

[95] Rudisill and Engelder: *J. Phys. Chem.*, **30**, 106 (1926).

cleavage of ketones.[96] Phosphoric acid prepared according to Ipatieff's method is a very versatile catalyst.

Arsenic is used as a catalyst in fluorination of organic halogen compounds.[71]

Antimony pentachloride, $SbCl_5$ (SO_4, Cu, Fe, As), and antimony trichloride, $SbCl_3$ (Oxychloride, SO_4, As, Fe), are well-known chlorination carriers. The pentachloride is used for chlorination of acetylene (page 328), and also used as a polymerization agent for styrene.[86]

Bismuth oxide, Bi_2O_3 (NO_3, As_2O_3), 3 per cent, is used as promoter for cobalt oxide, 97 per cent, as a catalyst in ammonia oxidation.[97] Hilditch and Hall [13] state that a catalyst, containing 95 per cent iron oxide and about 3 per cent bismuth oxide, was used for the same purpose in technical operations in Germany. Bismuth salts are used in the hydration of propylene and butylene to the corresponding alcohols.[98]

Vanadic acid, V_2O_5, is a well-known, commercial catalyst for the oxidation of SO_2 to SO_3, and for the oxidation of aromatic compounds. This catalyst is prepared, according to Jaeger and Bertsch, as follows: [99]

"100 parts of crude vanadic acid containing about 84 per cent of V_2O_5 and also SiO_2, iron and alkali as impurities, are treated with 460 parts of water, and 38.5 parts of 100 per cent NaOH are added. The resulting solution is dark-colored due to the presence of the impurities. Chlorine gas is then passed through the hot solution and this continued until the color turns brownish-yellow and does not show any further change. 11 parts of hydrogen chloride, in the form of a 10 per cent solution, are gradually added to produce neutrality to litmus and the solution is acidified with one part of nitric acid, the liquid being kept continuously at the boiling point. Ammonia water is then added until the lumps of vanadic acid have disappeared and the liquid gives off a distinct odor of ammonia. The solution is permitted to stand at an elevated temperature and all of the impurities can then be filtered out whereupon the light-green solution (540 volumes) is treated with from 50 to 70 parts of pure ammonium chloride in the form of a 30 per cent solution, the latter being kept hot. The mixture is vigorously stirred and permitted to cool gradually, resulting in the precipitation of small crystals of metavanadate which are removed by filtration. The crystal cake is then stirred with 200 parts of water, again filtered, and the washing continued until neither the wash water nor the crystals show any traces of chlorine. The yield of crystals is about 88–90 per cent of the theoretical and they consist of very pure ammonium metavanadate, showing no trace of iron.

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[96] McAllister, Bailey and Bouton: *J. Am. Chem. Soc.*, **62**, 3210 (1940).

[97] Scott: *Ind. Eng. Chem.*, **16**, 74 (1924).

[98] British Patents, 324,897 (1930) and 249,834 (1926).

[99] Jaeger and Bertsch: U. S. Patent, 1,765,870 (1930).

"The ammonium metavanadate is first heated in a muffle oven at temperatures of 200–300°C in a stream of air and then at 300–400°C in a stream of oxygen, the latter heating being continued for about two hours with stirring. The hot product is then permitted to cool in a stream of oxygen, producing vanadium pentoxide of practically 100 per cent purity and free from lower oxides.

"The mother liquors and wash liquors, from the process, constitute a very dilute vanadium-containing solution which can be heated until the solution becomes clear, and then sufficient hydrochloric acid added until the liquid is just alkaline, whereupon ammonia is added until its odor becomes clearly perceptible. The vanadium is precipitated with a 10 per cent solution of barium chloride, the addition taking place until a test shows no further precipitation with barium chloride. The barium compound of vanadium is then filtered, stirred to a slurry, and rendered acid to congo red with nitric acid, the product being stirred continuously. A red-brown vanadic acid precipitates out, amounting to about 6 per cent of the total vanadium content of the original crude vanadic acid. The recovered vanadic acid is added to the crude vanadic acid of the next batch. It will be seen that the total recovery of vanadium is about 96 per cent."

If, in a purified vanadic acid, almost free from the lower oxides of vanadium, iron and nitric acid are present, "the vanadic acid is dissolved in caustic soda solution and made just acid to litmus with hydrochloric acid. Hydrogen peroxide is added and a little chlorine is passed through at an elevated temperature, whereupon ammonia is added at 80 or 90°C, until the solution is just alkaline. The solution is stirred and permitted to settle, precipitating out the iron in fine flocks which can be removed by hot filtration. The hot filtrate is then worked up into ammonium metavanadate and vanadic acid as described above." It follows that the ammonium vanadate must be precipitated with iron-free ammonium chloride.

Bertsch[100] makes a sulfuric anhydride catalyst by treating 330 liters of 4–6 mesh granules of a carrier substance (Tripoli, Opalite, Carrara silicate, Geyserite) with an aqueous solution containing an equivalent of 12 kilograms of vanadium pentoxide and 20 kilograms of potassium hydroxide or a mixture of sodium and potassium hydroxides. After being dried, the product is calcined, in the usual manner, by passing acidic vapors (e.g., sulfur dioxide or sulfur trioxide) in contact with the mass, or by treatment with dilute acid solutions. The resulting product gives a conversion of sulfur dioxide to trioxide of 98.3–98.9 per cent in commercial loadings. Instead of pentavalent vanadium, tetra- or trivalent vanadium may be used and, if desired, other catalytically active elements, such as silver, copper, and aluminum, may be added. Thus, by making a preparation as just described and subsequently treating with a small amount of a soluble platinum or other noble metal a very active catalyst is claimed to result, the activity of which is above what it would be when either one of the reagents is employed alone. With such a catalyst, sulfur dioxide is converted to the trioxide at an efficiency of 97 per cent and above when the catalyst is made up substantially as follows:

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[100] **Bertsch: U. S. Patent, 1,933,091 (1933).**

330 liters of carrier
240 grams platinum
6 kilograms of vanadium pentoxide
6 kilograms of potassium hydrate

For sulfuric acid manufacture, the vanadium contact is less subject to poisoning than platinum metal contacts.

Vanadium oxides and compounds are also catalytic agents for other purposes of which some examples are: (1) conversion of methyl alcohol to formaldehyde;[101] (2) making oxalic acid from sucrose;[102] (3) oxidation of methane to formaldehyde;[103] dehydrogenation.[19, 104] Many other uses and references are reported.

Group VI: O (16, 17, 18), S (32, 33, 34), Se (74, 76, 77, 78, 80, 82), Te (122, 123, 124, 125, 126, 128, 130), Po.
Cr (50, 52, 53, 54), Mo (92, 94, 95, 96, 97, 98, 110) (Al, As, Ca, Cu, Fe, P, Si, Zn), W (182, 183, 184, 186) (As,

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[101] Canneri and Cozzi: *Chimica industria (Italy)*, **21**, 653 (1935).

[102] Tanz and Kao: *J. Chem. Eng., China*, **6**, 32 (1939); *Chem. Abstracts*, **35**, 5466 (1941).

[103] Kreskov: *J. Gen. Chem. (U.S.S.R.)*, **10**, 1605 (1940); *Chem. Abstracts*, **35**, 2885 (1941).

[104] Stanley: British Patent, 514,587 (1939).

Cb, Mo, P, S, Si, Ta, Ti, V, Zn), U (C, Ca, Cu, Fe, Mg, O, Si, V.)*

Sulfur, in the form of sulfur dichloride, is used in the chlorination of hydrocarbons, and also as a vulcanizing agent in the preparation of factice and in conditioning rubber. Sulfur, having a strong affinity for most of the chemical elements, is a strong catalyst poison. Sulfuric acid (Cl, NO_3, NH_3, SO_2, SO_3, Se, As_2O_3, Fe, traces of heavy metals, O) and acid sulfates (Cl, NO_3, As_2O_3, NH_3, Fe, traces of heavy metals) catalyze the polymerization of castor oil. Sulfur dioxide is a catalyst in the polymerization of styrene[105] and fatty oils.[106] Sulfuric acid with copper is a polymerization catalyst for acetylene.[42] Sulfuric acid is also used as an alkylating and polymerizing agent in the petroleum industry.

Chromium oxide, Cr_2O_3 (Cl, SO_4, NH_3, alkalies, Fe), for catalytic use, has been studied by Lazier and Vaughan,[107] who prepared Cr_2O_3 in various ways for hydrogenation of ethylene, propylene, and octylene, and for dehydrogenation of cyclohexane. Ammonium chromate, thermally decomposed at not too high a temperature so as to give an amorphous oxide, is the most active. Higher heating than leading to the formation of crystalline oxide greatly impaired or destroyed the catalytic activity for the aforementioned hydrogenations. The activity of Cr_2O_3 as catalyst for methanol synthesis or for dehydrogenation of ethanol is less affected by the formation of crystals.

Adkins, Folkers and Conner[50, 52] prepared copper-chromium oxide as follows:

900 cc of a solution at 80°C, containing 260 g of trihydrated copper nitrate and 31 g of barium nitrate are added to 900 cc of a solution at 25°C, containing 151 g of ammonium dichromate and 225 cc of

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[105] Dupont de Nemours, E. I., & Co.: British Patent 511,417 (1939).

[106] Waterman et al.: *Verkroniek*, **13**, 130, 180 (1940); *Chem. Abstracts*, **34**, 8305 (1940).

[107] Lazier and Vaughan: *J. Am. Chem. Soc.*, **54**, 3080 (1932).

* The numbers in parentheses indicate the various isotopes (see Ashton page 123). The elements and compounds in the parentheses are impurities which are listed in literature as having been found in the substance or substances in question.

28 per cent ammonium hydroxide. The precipitate is filtered, the cake pressed with a spatula, and sucked as dry as possible, then dried in an oven for 12 hours at 75 to 80°C and then pulverized. The powder is decomposed in three portions, in a casserole, over a free flame, under continuous stirring with a spatula, care being taken that the heating is so regulated that the evolution of gases does not become violent. This is accomplished by heating only one side of the casserole and stirring the powder more rapidly when the decomposition starts to spread throughout the mass. During this operation, the color of the powder changes from orange to brown and finally to black. When the entire mass has become black, and the evolution of gases has ceased, the powder is removed from the casserole and allowed to cool. The combined product is then leached for thirty minutes with 600 cc of a 10 per cent acetic acid solution, filtered, and washed with 600 cc of water in six portions, dried for 12 hours at 125°C, and pulverized. The yield of catalyst was 170 g. Copper sulfate and sodium dichromate may be substituted for the corresponding nitrate and potassium salts. A highly active and uniform catalyst of this type has been made on a semi-plant scale by Calingaert and Edgar.[108]

Lazier has studied chromite catalysts intensively and a student of this problem is referred to his work,[109, 110] of which only a very few examples can be dealt with here. For hydrogenation of aldehydes, ketones, sugars, phenols, furfural and its derivatives, benzene and pyridine and their homologs, Lazier [109] uses, as a catalyst in the liquid phase, a preparation made by reducing a combination of an oxide of one of the hydrogenating metals such as nickel, copper, cobalt, and iron, with a more acidic oxide, such as one of the elements contained in the fifth and sixth groups of the periodic system, typified by chromium.

The combined salts, corresponding to these oxides, are ignited and reduced with hydrogen, the object of this treatment being to obtain the hydrogenating component in the form of a finely-divided and highly-active metal or metallic oxide.

The catalysts thus prepared are resistant to catalyst poisons such as sulfur and oxygen. The poisoned catalyst is regenerated by gentle ignition followed by reduction.

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[108] Calingaert and Edgar: *Ind. Eng. Chem.*, **26**, 878 (1934).

[109] Lazier: U. S. Pat., 2,077,421 (1937).

[110] Lazier, W. A.: *Hydrogenation of the Oxides of Carbon—Progress in the Catalytic Hydrogenation of Fats and Oils*, Twelfth Report of the Committee of Catalysis, National Research Council, New York, John Wiley & Sons, 1940, pp. 120 and 131.

These catalysts can also be tabletted on an ordinary pharmaceutical tabletting machine for continuous operation.

Example 1: Nickel oxide or carbonate is digested with chromic acid until completely dissolved. On evaporating the solution to dryness, the residue is reduced with hydrogen, or is first heated to redness, representing a temperature in the vicinity of 800°C, to convert it into the chromite, followed by hydrogen reduction.

Example 2: 228 g of pure nickel hydroxide were suspended in water and treated with 200 g of chromic anhydride. The resulting paste was filtered, dried, and ignited 4 hours at 400°C. Five grams of the residual nickel chromite composition was reduced 24 hours with hydrogen at 500°C and added, without exposure to air, to 200 cc of crude synthetic alcohols boiling in the range 100–135°C, prepared by high-pressure dehydrogenation of ethanol, and containing, in addition to butanol, about 20 per cent of unsaturated compounds such as crotonyl alcohol and 30–40 per cent of esters, including butyl acetate and ethyl butyrate. After agitating the mixture for 2 hours at 150°C under a hydrogen pressure of 400 lb, the iodine value of the mixture had dropped from 99 to 33, indicating saturation of the compounds which contained unsaturated bonds, with a resultant improvement in the quality of the product for solvent purposes.

Example 3: 100 g of furfural and 13 g of water were shaken vigorously with 7 g of nickel chromite catalyst prepared by reduction of nickel chromate with hydrogen at 450–500°C under 1400 lb hydrogen pressure and at a temperature of 80–110°C. The yield of tetrahydrofurfuryl alcohol was about 65 per cent.

$ZnO—Cr_2O_3$ is a very effective methanol catalyst.[111] Cr_2O_3 is also used as a catalyst for dehydrogenation, dehydration, cyclization, and isomerization. Adadurov et al.[11] report that chromium does not adsorb hydrogen, and that by alloying chromium with platinum, the catalytic activity of the latter is not effected. However, the platinum becomes more stable toward hydrogen when alloyed with chromium.

Molybdenum trioxide, MoO_3 (lower oxides, Cl, NO_3, PO_4, SO_4, NH_3, traces of heavy metals), and molybdenum sulfide, MoS_2, are used as catalysts in destructive hydrogenation of coals, tars and oils (page 349). Methods for preparation of molybdenum trioxide have been studied by Bahr and Patrick.[112] Molybdenum is also used mixed with ammonia catalysts in hydrogenation, oxidation, polymerization, etc.

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[111] Larson: *Trans. Electrochem. Soc.*, 71, 345 (1937).

[112] Bahr and Patrick: *Brennstoff-Chem.*, 14, 161 (1933).

Tungsten oxide, WO_3, and tungsten sulfide, WS_3, are used in the destructive hydrogenation of oils,[113] in oxidation, dehydration of alcohols, hydration of ethylene, and as a metal or oxide in mixed catalysts.

Uranium carbide serves as a catalyst in ammonia synthesis below 500°C.[114] Uranium catalyzes the formation of hydrocyanic acid from a mixture of nitrogen, hydrogen, and carbon monoxide.[115] Uranium oxides are used as catalysts in oxidation and dehydrogenation, and colloidal uranium oxide, UO_3, is assumed to act as a catalyst in the synthesis of formaldehyde by the action of sunlight on a solution of carbon dioxide in water.[116]

Group VII: F, Cl (35, 37), Br (79, 81), I.
Mn, Ma, Re (185, 187).

The halogens and halides are important agents in ordinary synthesis and as catalysts. Chlorine is a catalyst for decomposition of ethyl chloroformate.[117] Bromine and iodine are active catalysts in the decomposition of acetaldehyde.[118, 119] Iodine catalyzes the addition of HI to unsaturated compounds,[120] the isomerization of dichloroethylene,[121] and the thermal decomposition of acetone.[122] The highly reactive hydrofluoric acid, HF, is now used in considerable amounts as a fluorinating agent, as a catalyst for polymerization and acylation,[123] and as a condensing agent.[124] The applications of the halides, as catalytic agents, have been dealt with in detail by Thomas et al.[79] and Burk.[125]

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[113] Johnson: British Patent, 379,335 (1932).

[114] Haber: *Z. Elektrochem.*, **16**, 244 (1910).

[115] Beindl: U. S. Patents, 1,492,193 and 1,492,194 (1924).

[116] Moore and Webster: *Proc. Roy. Soc., London*, **87 B**, 163 (1913); *ibid.*, **90 B**, 168 (1919).

[117] Choppin and Kirby: *J. Am. Chem. Soc.*, **62**, 1592 (1940).

[118] Fromherz: *Z. phys. Chem.*, **B 25**, 301 (1934).

[119] Hinshelwood, Clusius and Hadman: *Proc. Roy. Soc., London*, **A 128**, 88 (1930).

[120] Kharasch, Norton and Mayo: *J. Am. Chem. Soc.*, **62**, 81 (1940).

[121] Wood and Dickinson: *J. Am. Chem. Soc.*, **61**, 3259 (1939).

[122] Gantz and Walters: *J. Am. Chem. Soc.*, **62**, 996 (1940).

[123] Simonds: *Ind. Eng. Chem.*, **32**, 332, 178 (1940).

[124] Simonds, Passins and Archer: *J. Am. Chem. Soc.*, **63**, 608 (1941).

Manganese acetate is used for conversion of acetaldehyde to acetic acid (page 325). MnO_2 is the catalyst in the Weldon process for making chlorine and also for various oxidations. A notable use of manganese salts is as "driers" in vegetable oils for the paint and varnish industry. MnO is a catalyst for preparation of ketones from fatty acids.[126] For this purpose, $MnCO_3$ is adsorbed on pumice and heated in a current of nitrogen at 400–450°C for eight hours. Manganese vanadate, $Mn_3(V_3O_9)_2$, mixed with zinc vanadate, $Zn_3(VO_4)_2$ (1:4), is a catalyst for preparation of acetone from acetylene and water.[127]

Rhenium is a catalyst for dehydrogenation of butyl alcohol,[128] and for hydrogenation of coal-tars and petroleum.[128a] In the latter case, rhenium or its compounds are adsorbed from colloidal suspensions on powdered activated charcoal, powdered coal, or similar material. The catalytic properties of rhenium have been described by several authors.[129, 130, 131]

Group VIII: Fe (54, 56) (Ag, Al, As, B, Bi, C, Ca, Co, Cu, Cd, Cr, Ga, Mg, Mn, Mo, Ni, P, Pb, S, Si, Sn, Sb, Ti, V, W, Zn, Zr), Co (As, C, Ca, Fe, Mn, Ni, P, S, Si), Ni (58, 60) (Al, As, B, C, Ca, Co, Cr, Cu, Fe, Mg, Mn, Na, Pb, Si, Sn, Zn).*

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[125] Burk, R. E.: *Halide Catalysts*, Twelfth Report of the Committee of Catalysis, National Research Council, New York, John Wiley & Sons, Inc., 1940, p. 251.

[126] Cowan, Jeffrey and Vogel: *J. Chem. Soc.*, **171** (1940).

[127] Cozzi: *Atti X°., congr. intern. chim.*, **3**, 89 (1939); *Chem. Abstracts*, **34**, 982 (1940).

[128] Platonov and Anisimov: Russian Patent, 52,780 (1938); *Chem. Abstracts*, **34**, 5467 (1940).

[128a] Bataafsche, N. V. de, Petroleum Mataschappij: German Patent, 693,707 (1940).

[129] Platonov: *J. Gen. Chem. (U.S.S.R.)*, **11**, 590 (1941); *Chem. Abstracts*, **35**, 6924 (1941).

[130] Zenghelis and Stathis: *Compt. rend.*, **209**, 797 (1939).

[131] Zenghelis and Stathis: *Kolloid Ztg.*, **90**, 129 (1940); *Chem. Abstracts*, **34**, 2678 (1940).

* The numbers in parentheses indicate the various isotopes (see Ashton page 123). The elements and compounds in the parentheses are impurities which are listed in literature as having been found in the substance or substances in question.

Ru (96, 98, 99, 100, 101, 102, 104), Os (186, 187, 188, 189, 190, 192).
Rh, Ir, Pt.

Iron is one of the most common impurities in all chemicals and it is also a very important catalyst, especially in ammonia synthesis. Due to its cheapness, it may gain further ground in mixed catalysts, especially for making contact masses which can be discarded after being used catalytically.

Iron catalysts, for ammonia synthesis, are discussed on pages 31, 310 and it should be added that the reduced iron catalyst may be prepared from either the precipitated hydrous oxide or from the oxide made by calcining the nitrate. Ammonia catalysts have been discussed in detail by Frankenburger [132] and Emmett et al,[133, 134] who report recent developments. When preparing iron oxides for catalytic use, the temperature for either dehydrating or calcining the oxide should be the lowest possible, and according to Sabatier and Mailhe,[135] the dehydration temperature should be below 350°C. However, it takes between 400 and 500°C from seven to six hours, to reduce the iron oxide in a hydrogen atmosphere,[136] and usually the reaction temperatures are higher for iron than for the other metals of the eighth group. Iron catalysts may also be made from Fe-Al alloys similarly to Raney nickel, in which case, the iron powder is pyrophoric.[136] Bosch [137] states that iron, due to its richness in spectral lines should be very promising as a catalyst. Mittasch [138] found that magnetite from Gellivare in Sweden was a good ammonia catalyst but magnetites from other places were not as good. The composition of the Swedish magnetite was as follows: 20 g Fe + 0.2 g CaO + 0.1 g Al + 0.1 g MnO + 0.1 g MgO + 0.1 g Co_2O_3.

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[132] Frankenburger: *Z. Elektrochem.*, **39**, 45, 97, 269, 818 (1933).

[133] Emmett et al.: *J. Am. Chem. Soc.*, **55**, 1738 (1933); *ibid.*, **56**, 35 (1934); *ibid.*, **57**, 1624, 1631, 1754, 2732 (1935).

[134] Emmett, P. H.: *The Synthesis of Ammonia*, Twelfth Report of the Committee of Catalysis, National Research Council, New York, John Wiley & Sons, Inc., 1940, p. 138.

[135] Sabatier and Mailhe: *Ann. chim. phys.*, (**8**), **20**, 313 (1910).

[136] Paul and Hilley: *Compt. rend.*, **206**, 608 (1938).

[137] Bosch: *Z. Elektrochem.*, **24**, 367 (1918).

[138] Mittasch: *Ber.*, **59**, 19 (1926).

Iron catalysts, to which have been added small amounts of mild alkalies (CaO, K_2CO_3), are used in the single-stage process for production of acetone from alcohol or acetylene and steam, and for the preparation of higher alcohols from water gas.

Iron chloride is used as a chlorination catalyst for chlorination of benzene and toluene,[139] and as a dechlorination catalyst in hydrogen halide removal from halo nitriles.[140] Iron is also used in conjunction with cobalt and manganese as a drier in paints and varnishes containing fish oils.[60] Small amounts of iron or its compounds are extremely important oxidation catalysts in nature and in living organisms.

Cobalt has catalytic properties, to some extent, between those of iron and nickel. Its oxide is reduced at 400°C. Its catalytic power in hydrogenation is not as great as that of nickel, but greater than that of iron.[84] Physical conditions play an important part in this property, and any generalization should be taken with some reserve (Lohse). Cobalt catalysts, prepared from precipitated cobalt hydroxides, have higher activity than those prepared by reduction of the oxides.[62]

Cobalt-thoria catalysts are important in the production of gasoline from water gas[141] (see page 151). Cobalt oxides, Co_2O_3 and Co_3O_4, are used as oxidation catalysts. Organic cobalt salts are catalysts in the oxidation of paraffins for the production of fatty acids.[142] Organic cobalt salts, when decomposed, serve as a basis for preparation of cobalt oxides and reduced cobalt for catalytic purposes.[143] Cobalt-Magnesium catalysts are prepared by precipitation of a mixture of their nitrates or chlorides. The precipitation should be rapid. The magnesium is used in 25–75 per cent excess.[144]

Cobalt compounds are extensively used as driers (oxidation catalysts) in paints and varnishes, constituting the most active catalysts for this purpose. Cobalt, as a drier, is either used alone or with an auxiliary metal compound such as a compound of lead or zinc.[60, 66] Originally cobalt was added as a resinate and then as an oleate. These driers are now superseded by cobalt linoleates. A typical linoleate paste contains 6 per cent cobalt, and a linoleate liquid 4 per cent cobalt. Where rapid finishes are required, naphthenate driers are used, containing about 12 per cent cobalt. Cobalt is chiefly a surface drier, and manganese is added for drying the body of the paint.[145]

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[139] German Patent, 219,242 (1907).

[140] Loder: U. S. Patent, 2,175,810 (1940).

[141] Fischer and Koch: *Brennstoff-Chem.*, 13, 61 (1932).

[142] Hicks and Brunn: U. S. Patent, 2,249,708 (1941).

[143] British Patent, 315,818 (1929).

[144] N. V. Int. Koolwaterstoffen Maatschappij: Dutch Patent, 51,204 (1941); *Chem. Abstracts*, **36**, 4298 (1942).

Metallic nickel, in finely-divided form or in the form of an oxide, or a mixture of both, is one of the most important catalytic contact agents. For preparation and activation of such catalysts, a great many methods have been proposed.[157] The major nickel sources, for making nickel catalysts, are metallic nickel, nickel-aluminum alloys, nickel sulfate, nickel formate, nickel carbonate, nickel oxide, and nickel nitrate. To this should be added spent nickel catalyst which is also an important source of catalytic nickel.

Nickel sulfate, $NiSO_4, 7H_2O$ (Cl, NO_3, alkalies, alkaline earths, Co, Cu, Fe, Zn, traces of heavy metals), contains about 20 per cent nickel and when used for making hydrogenation catalysts, it is precipitated as basic nickel carbonate with soda ash, sodium bicarbonate, or ammonium carbonate, the precipitate being washed free from sulfate as far as possible. The dried carbonate may be reduced directly and used as a catalyst, a rotating reducing furnace, with exact temperature control, being used. The furnace consists of a rotating steel tube, the catalyst being carried along, inside of this tube, by means of a helical conveyor ribbon welded to the inside of the tube. Means are provided for feeding in the unreduced catalyst at a predetermined rate and also for discharging the finished catalyst into oil without coming into contact with air.[145a]

When the carbonate is to be reduced directly, the nickel sulfate is mixed with kieselguhr (diatomaceous earth) and the basic nickel carbonate is precipitated on the kieselguhr particles. This

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[145] *Data Book on Nickel and Cobalt Oxides and Salts. Selenium, Tellurium,* London, Henry Wiggins and Co., Ltd., 1939.

[145a] Sieck: *Oil & Soap,* **16**, 24 (1939).

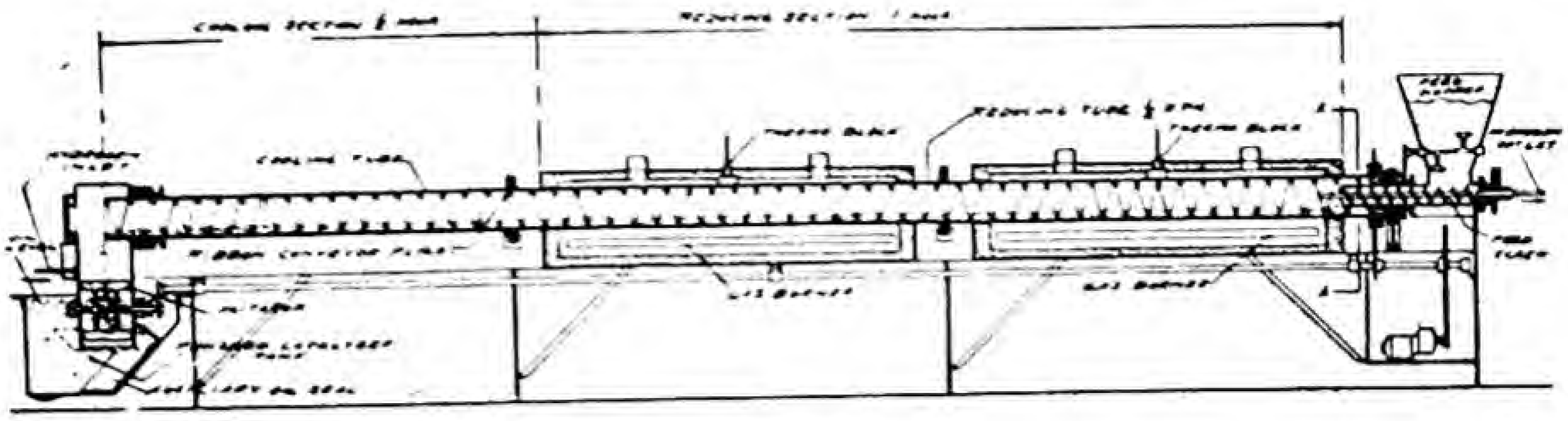

FIGURE 10

CROSS SECTION OF A CONTINUOUS CATALYST REDUCING FURNACE
(Courtesy of Sieck & Drucker, Inc., Chicago, Ill.)

process should be regulated so that the nickel content, in the finished product, is at least from 12 to 15 per cent, and the content of metallic nickel, in the reduced catalyst, is as high as possible. Ammonium carbonate is a preferred precipitant as far as activity is concerned, because it is volatile, i.e., readily removable.[50] The basic nickel carbonate may also be converted into a salt of an organic acid, such as formic, oxalic, lactic, or acetic acid, these salts being readily reduced in the oil.

Nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O(Cl, SO_4, Fe, Co)$, contains about 20 per cent nickel, and is an ideal source of highly-active nickel catalysts. The nitrate is calcined yielding a nickel oxide, and when metallic nickel is desired, the oxide is reduced with hydrogen. The reduction yields a very good hydrogenation catalyst. The nickel nitrate may also be used as above, being precipitated as basic nickel carbonate, although that is a more expensive process.

Nickel carbonate, $NiCO_3$, containing about 49 per cent nickel, is obtained by adding sodium bicarbonate to a cold nickel nitrate solution and saturating with carbon dioxide. The precipitate, formed when alkali carbonates are added to a nickel salt solution, consists of a basic carbonate of varying composition, e.g., $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$ (about 50 per cent nickel).

Nickel oxides.[25, 74, 146, 147] The composition of the nickel oxides

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[146] Mellor, J. W.: *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London, Longmans, Green & Co., 1935, p. 844.

[147] Moissan: *Ann. chim. phys.*, 5, 21 (1880).

is somewhat disputed. The stoichiometrical formulas usually encountered are the following:

Nickel monoxide, NiO, green
Nickel sesquioxide, Ni_2O_3, black (mixture of NiO and NiO_2?)
Nickel oxide (ous) (ic), Ni_3O_4, gray (magnetic)
Nickelic hydroxide, $Ni(OH)_3$, black (existence doubtful)
Nickelous hydroxide, $4Ni(OH)_2 \cdot H_2O$, light green
Nickel dioxide, NiO_2

Ni_2O_3 is converted quantitatively into Ni_3O_4 at 190°C, and at 200°C, the green or yellow oxide, NiO, is formed, which is reduced to metallic nickel at 230 to 240°C. This nickel is pyrophoric, burning in air to Ni_2O_3. NiO at 355 to 440°C is converted into Ni_2O_3, which begins to decompose above 440°C, NiO being again obtained at 600°C. Ipatieff [74] asserts that the oxide Ni_2O_3 does not exist, and the black and brown nickel oxides represent mixtures of nickel oxides, probably of NiO with some higher oxide of nickel, e.g., NiO_2. This is a matter which requires further elucidation.[74a] Ipatieff uses nickel oxides as hydrogenation catalysts, the temperature and pressure generally being higher than with metallic nickel catalysts (e.g., 250°C, and 100 atm. pressure). One advantage of using the oxides is that they are much less sensitive to catalyst poisons such as S, Cl, and CO than the metallic catalysts. In judging the activity of the nickel oxides as catalysts, it should be borne in mind that they sinter readily.[148]

The pyrophoric character of finely divided nickel, obtained by reducing nickel oxide in a current of hydrogen, is due to occluded hydrogen, which, on contact with the active nickel, is activated so that it combines with the oxygen of the air. By treating the reduced nickel with a current of pure CO_2 or N_2 its pyrophoric property disappears. However, if the nickel so treated is heated in a current of hydrogen again it becomes pyrophoric. The pyrophoric property of nickel is not a measure of its catalytic activity.

Of the organic nickel salts, nickel formate is most widely used as a commercial hydrogenation catalyst for vegetable and animal oils. It is one of the simplest nickel catalysts to prepare. Wurster[149] has described this procedure in detail. Nickel formate, which should preferably be very finely ground, is mixed under continued stirring with the oil to be hydrogenated in a catalyst reducer (see figure 11, p. 156), the ratio of oil to formate being 1:1, if the finished catalyst is to be shipped, and up to 4:1, if the reduced catalyst is pumped from the reducer directly into the converter. In the first case, the nickel content of the finished catalyst is about 23 per cent, and in the latter case about 7 per cent. The oil and the catalyst are kept mixed by agitation.

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[148] Boswell and Iler: *J. Am. Chem. Soc.*, **58**, 924 (1936).

The thermal decomposition of the nickel formate is claimed to take place according to the following equation:

$$(HCOO)_2Ni \cdot 2H_2O \rightarrow Ni + 2CO_2 + H_2 + 2H_2O$$

This decomposition begins at 150°C, and at this temperature, or already at 130 to 140°C, the introduction of hydrogen is begun, the reducer being vented all the time. According to the equation, for each pound of nickel 5.5 cubic feet of carbon dioxide and hydrogen, and 3.9 cubic feet of steam are given off, so that a total of about 9.4 cubic feet of gases is to be vented.

The steam, from the water of crystallization, escapes vigorously around 190°C and the oil starts to harden. When the steam is driven off, the temperature rises rapidly to 240 to 250°C, to a point where the oil smokes considerably. In order to get good activity, the charge is kept at this temperature for half an hour to one hour. At the higher temperature limit, the shorter time is required. Freshly precipitated nickel formate reduces more readily at low temperature, which undoubtedly occurs if the freshly precipitated formate is finely dispersed in the oil. Generally, it seems that the finer the dispersion of the formate the better is the activity of the resulting catalyst.

It is claimed that the reduction of the nickel formate is a purely thermal decomposition independent of the added hydrogen. Whereas this may be true in principle, there is no doubt that the

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[149] Wurster: *Ind. Eng. Chem.*, **32**, 1194 (1940).

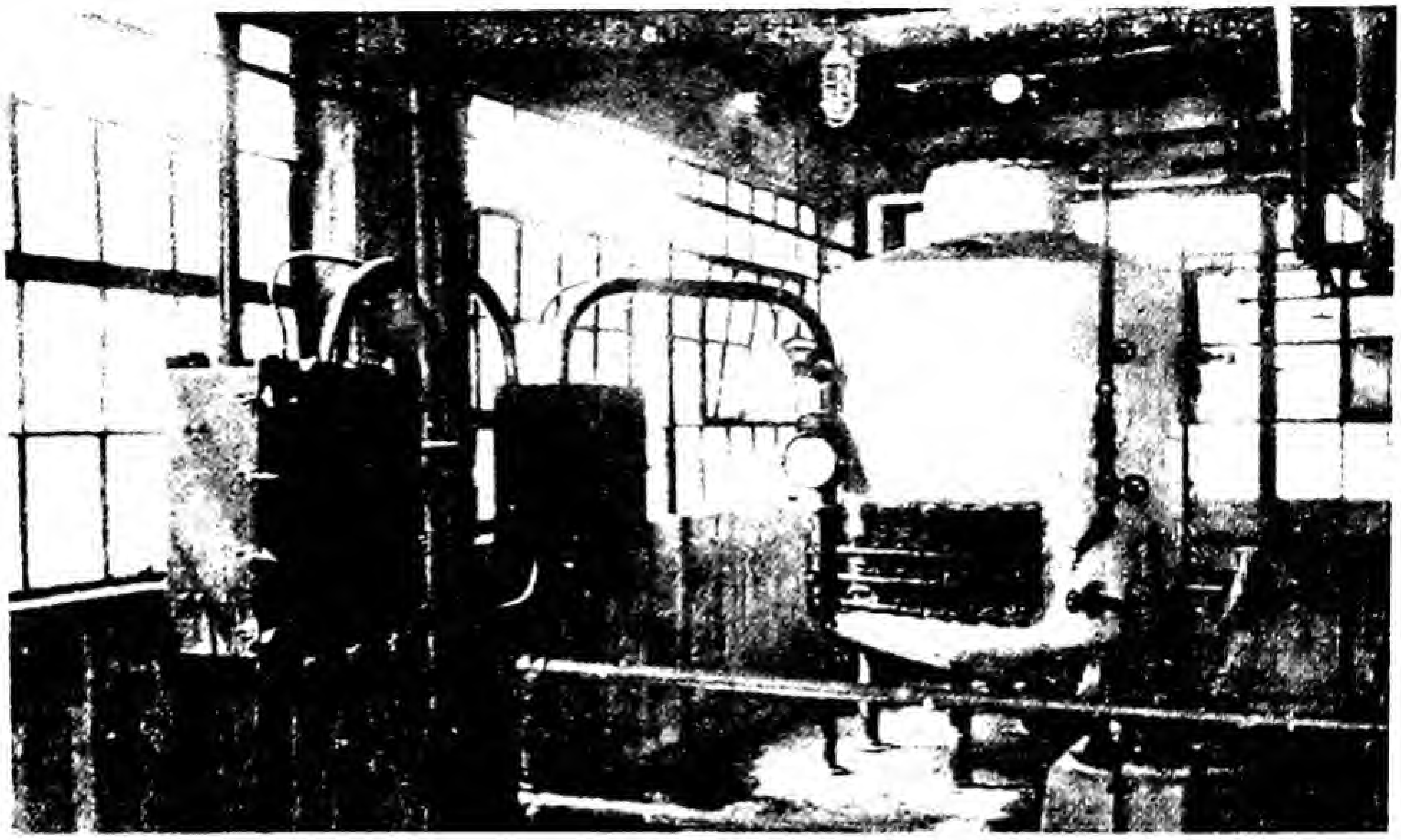

FIGURE 11

WURSTER & SANGER CATALYST PLANT FOR WET REDUCTION OF NICKEL FORMATE
(Courtesy of Wurster & Sanger, Inc., Chicago, Ill.)

presence of steam causes formation of a considerable quantity of nickel oxide, which is again reduced, although partially only, to metallic nickel around and above 240° C, leaving a catalyst consisting of 60 to 70 per cent of oxide, the balance being metallic nickel:

$$Ni + 2H{\cdot}OH \rightarrow Ni(OH)_2 + H_2$$

$$Ni(OH)_2 \rightarrow NiO + H_2O$$

This mechanism requires further study.

In this connection, it should be noted that experiments by Dobychin et al.[150] have shown that in obtaining catalysts from nickel formate at 150 to 300°C, in vacuo and in a current of hydrogen, the latter were as much as five times as active as the

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[150] Dobychin: *J. Phys. Chem., (U.S.S.R.)*, **14**, 1151 (1940); *Chem. Abstracts*, **35**, 3882 (1941).

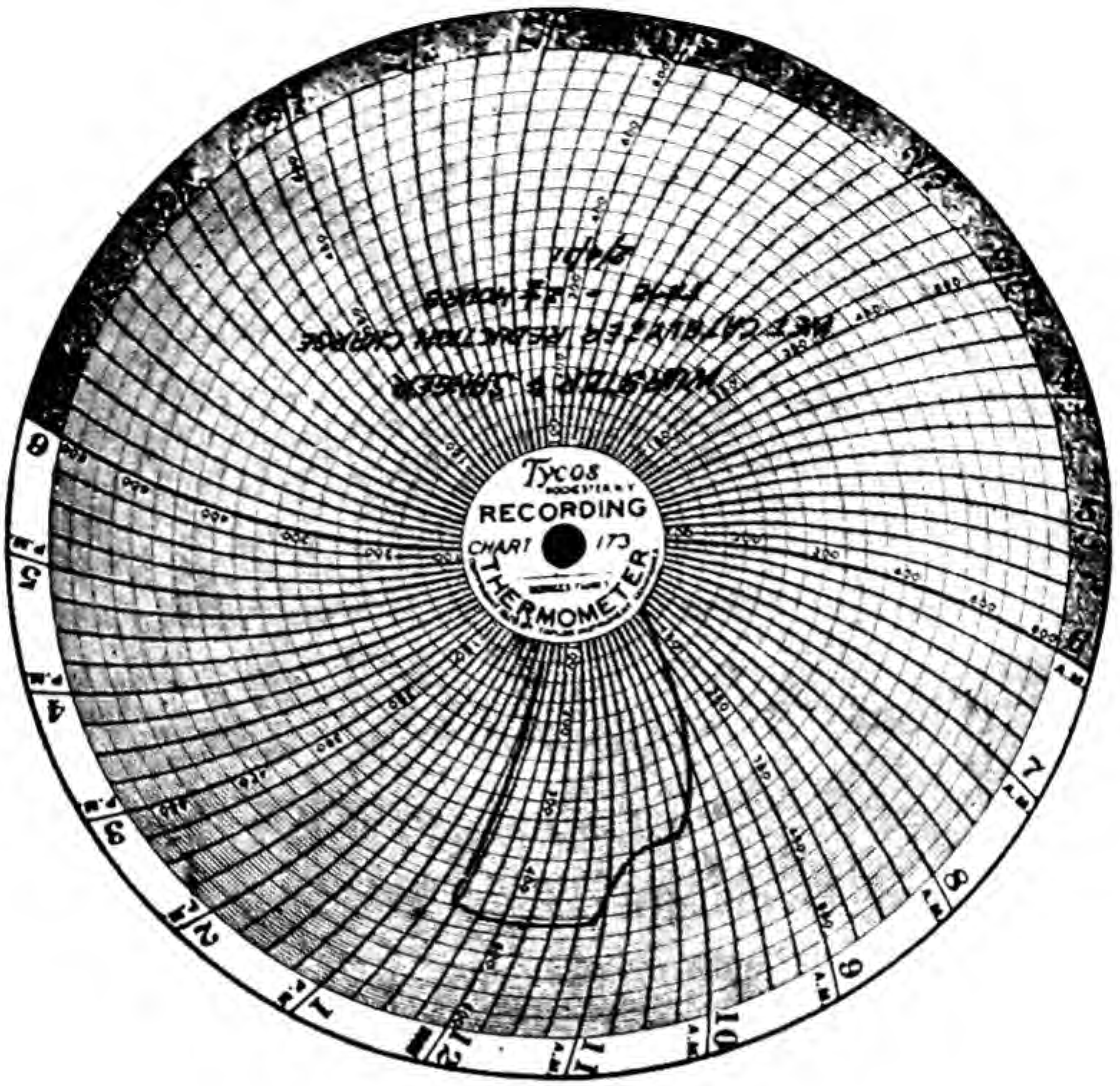

FIGURE 12

Temperature Record of the Reduction of Nickel Formate in Oil at a Maximum Temperature of 464°F (Wurster). (Reprinted by permission from *Ind. Eng. Chem.*, 32, 1195, 1940).

former. Furthermore, catalysts prepared from nickel formate, suspended in oil, are more active than those prepared from the dry salt as above, the reason being that the oil produces a more disperse catalyst by hindering recrystallization and sintering. In the dry decomposition of the nickel formate, the activity of the catalyst increases up to 245°C. Heating above this temperature gives a less active catalyst due to rapid aging. The increase in activity between 220 and 245°C was two to three fold. It was also found that the temperature should be brought up to the optimum as fast as possible.

In another study[150] the nickel formate was made as a paste with oil, preheated to 250°C, and reduced by dry hydrogen. It is claimed that this gives a more active catalyst than when the formate-oil mixture is slowly heated.

The decomposition of nickel formate has also been studied by Balandin et al.[151] who concluded that nickel catalysts obtained by decomposition of the formate in oil are catalytically active, but those obtained by decomposition in air or nitrogen are almost inactive.

Nickel catalysts may also be prepared by alloying nickel with other elements which are removable by water, weak acids, or alkali. Examples are alloys of nickel with Al,[45, 152] Si,[153] Na or Ca,[45] or Mg.[154] The nickel-aluminum catalysts developed by Raney[155] have found extensive use in the hydrogenation of vegetable and marine oils as well as in the hydrogenation of organic compounds.[50] According to Raney, the alloys containing 50% Ni + 50% Al, 42% Ni + 58% Al, and 30% Ni + 70% Al, are the most useful combinations. These alloys correspond approximately to the compositions $NiAl_2$, $NiAl_3$, and $NiAl_5$, although these compounds may not actually exist.[155a] The molten catalyst alloy is poured on a cooling table and converted into a powder. The aluminum is dissolved in alkali, usually in 20 per cent NaOH, the catalyst powder reacting readily with the cold solution with liberation of hydrogen. The heat generated by the reaction brings the liquid to a boil. The water, escaping as steam, is replaced in order to maintain the volume of the solution. Finally the mass is digested for two or more hours at 118–120°C. The nickel sludge in the tank is washed free from lye with cold water. Raney[155] states that "large quantities of sulfates and chlorides in the wash water apparently do not signify inferior quality in the catalyst." The catalyst is dried in a tank by adding oil, heat, and agitating until the drying is complete. Throughout the handling of the catalyst, it must be covered with water or the compound used for hydrogenation.

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[151] Balandin, Grigoryan and Yanysheva: *Acta Physicochim., U.S.S.R.,* **12,** 737 (1940); *Chem. Abstracts,* **35,** 960 (1941).

[152] Raney: U. S. Patent 1,628,190 (1927).

[153] Canadian Patent, 266,469 (1926).

[154] I. G. Farbenindustrie, A.-G.: German Patent, 408,811 (1925).

[155] Raney: *Ind. Eng. Chem.,* **32,** 1199 (1940); U. S. Patents 1,563,587 (1925); 1,628,190 (1927); 1,915,473 (1933).

[155a] Bradley and Taylor: *Proc. Roy. Soc. (London),* **159,** 56 (1937).

FIGURE 13

NICKEL COMPOUNDS FOR CATALYTIC USE

I. Nickel nitrate. II. Nickel formate. III. Reduced nickel catalyst in hardened oil. IV. Reduced nickel catalyst suspended in water.

The nickel oxide content in the Raney catalyst is negligible, the presence of oxides being precluded by the reducing action of the nascent hydrogen, generated when dissolving the aluminum out in the lye solution. Raney suggests that the nickel may be present in the form of NiH_2. The particle size of the nickel sludge is approximately 167 mesh, this nickel being pyrophoric at ordinary temperature. For activating nickel for laboratory work, a very good laboratory method has been described by Adkins and Covert.[156]

Many other methods have been suggested for the preparation of nickel catalysts for hydrogenation and these have been discussed at length by Ellis [157] and Fraser.[29]

The nickel catalysts prepared by Fischer et al.[22, 158] are mentioned partly because their research throws light on many of the problems encountered in preparing catalysts, and partly because these catalysts are very important. Nickel catalysts, as prepared by these authors, convert CO and H_2 to methane and liquid products (page 329). For this, the presence of an activator is necessary, the most favorable one being thoria, and also the simultaneous presence of kieselguhr, which appears to play a part in this conversion. The nickel is precipitated from a salt solution by an alkali carbonate, potassium carbonate being the best. The addition of 18 per cent thoria gives the best results, and the ratio of kieselguhr to the metal should be 1 : 1. The contact mass gives best results when reduced at 450°C. Addition of copper does not lower the reduction temperature. Such a catalyst gives 120 cc of liquid hydrocarbons, gas oil (Gasol) not included, calculated on the total consumption of CO (65 per cent CO was converted into liquid, and 35 per cent into gaseous hydrocarbons). The contact has a long life, losing only 17 per cent of its activity in five weeks. Data from differently prepared nickel contacts for the Fischer-Tropsch synthesis, as described, are listed on page 161.[158]

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[156] Adkins and Covert: *J. Am. Chem. Soc.*, **54**, 4116 (1932).

[157] Ellis, C.: *Hydrogenation of Organic Substances*, New York, Van Nostrand Co., 1930.

[158] Fischer and Meyer: *Brenstoff-Chem.*, **12**, 85 (1931).

Neumann and Jacob[24] made a very interesting study of supported nickel catalysts for conversion of carbon oxides into methane. Nickel nitrate, without a trace of sulfate or chloride, was soaked into the carrier, calcined at 550–600°C, and the oxide reduced below 280°C. Above this reduction temperature, the activity decreased due to sintering. The reduction was continued until a calcium chloride tube did not increase further in weight.

Several carriers were tried. Pumice and asbestos gave slow catalysts because the nickel surface soon became deactivated on account of the combination of the nickel with the silicate. A much better support was obtained from porous, unglazed, burned clay in pieces of 3 mm grain size boiled out in nitric acid, dried, dropped into the crystal water melt of the nitrate, ignited for two hours at 580°C, and reduced for 13 hours at 280°C. The nickel content of the finished product was approximately 20 per cent. The nickel penetrated 1–2 mm into the support. This catalyst gave good service at lower temperatures, but at higher temperatures, combination of the nickel with the silica in the support decreased the activity. For higher temperatures, pieces of magnesia tubes were treated as described for the clay support, and a very useful cata-

Nickel Contacts for the Fischer-Tropsch Synthesis

Experiment No.	Composition of the contact	Addition of kieselguhr	Method of preparation	Reduction temperature, °C	Necessary working temperature	Hours of reaction	Activity in per cent contraction	Per cent CO converted
1	Ni	no	heating the nitrate	350	230	18	1	..
2	Ni	yes	heating the nitrate	350	230	18	12	..
3	Ni	no	precipitating with Na_2CO_3	350	230	18	1.5	..
4	Ni	yes	precipitating with Na_2CO_3	350	220	42	24	25
5	9Ni + 1Ag	no	heating the nitrate	350	250	18	3	..
6	9Ni + 1Bi	no	heating the nitrate	350	250	18	3	..
7	99Ni + 1Cu	no	heating the nitrate	350	250	18	3	..
8	9Ni + 1Ag	yes	precipitating with Na_2CO_3	350	240	40	32	..
9	9Ni + 1Bi	yes	precipitating with Na_2CO_3	350	240	40	0	..
10	99Ni + 1Co	yes	precipitating with Na_2CO_3	350	240	40	19	..
11	Ni + 15% Al_2O_3	no	heating the nitrate	350	220	69	29	40
12	Ni + 15% Al_2O_3	yes	heating the nitrate	350	220	69	39	48
13	Ni + 15% Al_2O_3	yes	precipitating with Na_2CO_3	350	220	40	11	..
14	Ni + 18% ThO_2	no	heating the nitrate	350	260	70	7	..
15	Ni + 18% ThO_2	yes	heating the nitrate	350	260	70	30	..
16	Ni + 18% ThO_2	no	precipitating with Na_2CO_3	350	180	42	14	..
17	Ni + 18% ThO_2	yes	precipitating with Na_2CO_3	350	180	42	40	43
18	18% ThO_2	yes	precipitating with Na_2CO_3	350	190	163	46	54
19	18% ThO_2	yes	precipitating with Na_2CO_3	450	178	40	62	76
20	(9Ni – 1Cu) + 18% ThO_2	yes	precipitating with Na_2CO_3	350	188	93	16	17
21	Ni + (18% ThO_2 + 15% Al_2O_3)	yes	precipitating with Na_2CO_3	350	182	90	7.5	..
22	Ni + 18% ThO_2	yes	precipitating with $(NH_4)_2CO_3$	350	182	90	26.5	..
23	Ni + 18% ThO_2	yes	precipitating with $(NH_4)_2CO_3$	350	192	114	44	55
24	Ni + 18% ThO_2	yes	precipitating with NaOH	450	190	45	3.8	..
25	Ni + 18% ThO_2	yes	precipitating with KOH	450	180	40	0	..
26	Ni + 18% ThO_2	yes	precipitating with K_2CO_3	450	170	41	61	75
27	Ni + 18% ThO_2	yes	precipitating with K_2CO_3	450	175	41	65	85
28	18% ThO_2	yes	precipitating with K_2CO_3	450	180	138	65	84
29	Ni + 18% ThO_2	yes	precipitating with K_2CO_3	450	178	90	70	88
30	Ni + 18% ThO_2	yes	precipitating with K_2CO_3	450	170	54	44	60
31	18% ThO_2	yes	precipitating with K_2CO_3	450	180	117	48	..

lyst resulted. With 6.6 g of nickel on 45 g of MgO the reaction: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, was nearly quantitative at 300°C.

All the platinum group metals possess unique catalytic properties, those having the widest catalytic use being platinum, palladium and rhodium. The impurities, in the platinum metals, are about the same for the group, and are expressed by the general formula Pt (Ag, Au, Ca, Fe, Mg, Pb, Si, platinum metals) for metals of ordinary commercial purity.[159]

Platinum, deposited on carriers such as silica gel, magnesium sulfate, or asbestos, is used for the manufacture of sulfuric acid by the contact process. The early work on platinum as a commercial catalyst for the contact sulfuric acid process dates back to Knietch (1901).[160] The use of platinum, as a catalyst for oxidation of ammonia, is of immense importance. In order to show the extension of use of platinum catalysts, the following list of catalysts offered for the market by Baker & Co., Inc., is given:[161]

1. Platinum catalysts for high-temperature reactions:
    - Platinum gauze
    - 95%-platinum 5%-rhodium gauze
    - 90%-platinum 10%-rhodium gauze
2. Carrier-free platinum catalysts of high activity:
    - Platinum black
    - Platinum oxide (Adam's catalyst; 80–81 per cent Pt)
3. Platinum catalysts for reactions in the gaseous phase:
    - Platinum asbestos, 5 or 10 per cent
    - Platinum charcoal, 8 to 14 mesh, 0.5 or 1 per cent
    - Platinum silica gel, 0.3 per cent
    - Platinum on Alfrax, 0.5 per cent
    - Platinum on alumina pellets, 0.5 per cent
    - Platinum on Pyrex glass fibre, 5 per cent
4. Platinum catalysts for reactions in the liquid phase, especially hydrogenation at room temperature and atmospheric pressure:
    - Platinum on activated charcoal powder, 5 or 10 per cent
    - Platinum on alumina powder, 5 per cent

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[159] Baker & Co., Inc.: *Private Communication*, March 4, 1944.

[160] Knietch: *Ber.*, **34**, 4069 (1901).

[161] *Platinum Metal Catalysts*, Baker & Co., Inc., Newark, N. J.

Platinum on calcium carbonate, 5 per cent
Platinum on zinc carbonate, 5 per cent
Platinum gelatin colloid, 3 per cent solution

Platinum-rhodium alloys for ammonia oxidation were developed by du Pont and Baker,[162, 162a] and such alloy catalysts are now produced on a very large commercial scale.[164] The main advantages of using these catalysts are a higher conversion efficiency and a lower catalyst loss. In this connection, the following curves taken from a booklet published by Baker & Co., Inc., showing the advantages obtained by platinum-rhodium catalysts as compared with platinum, are of interest:

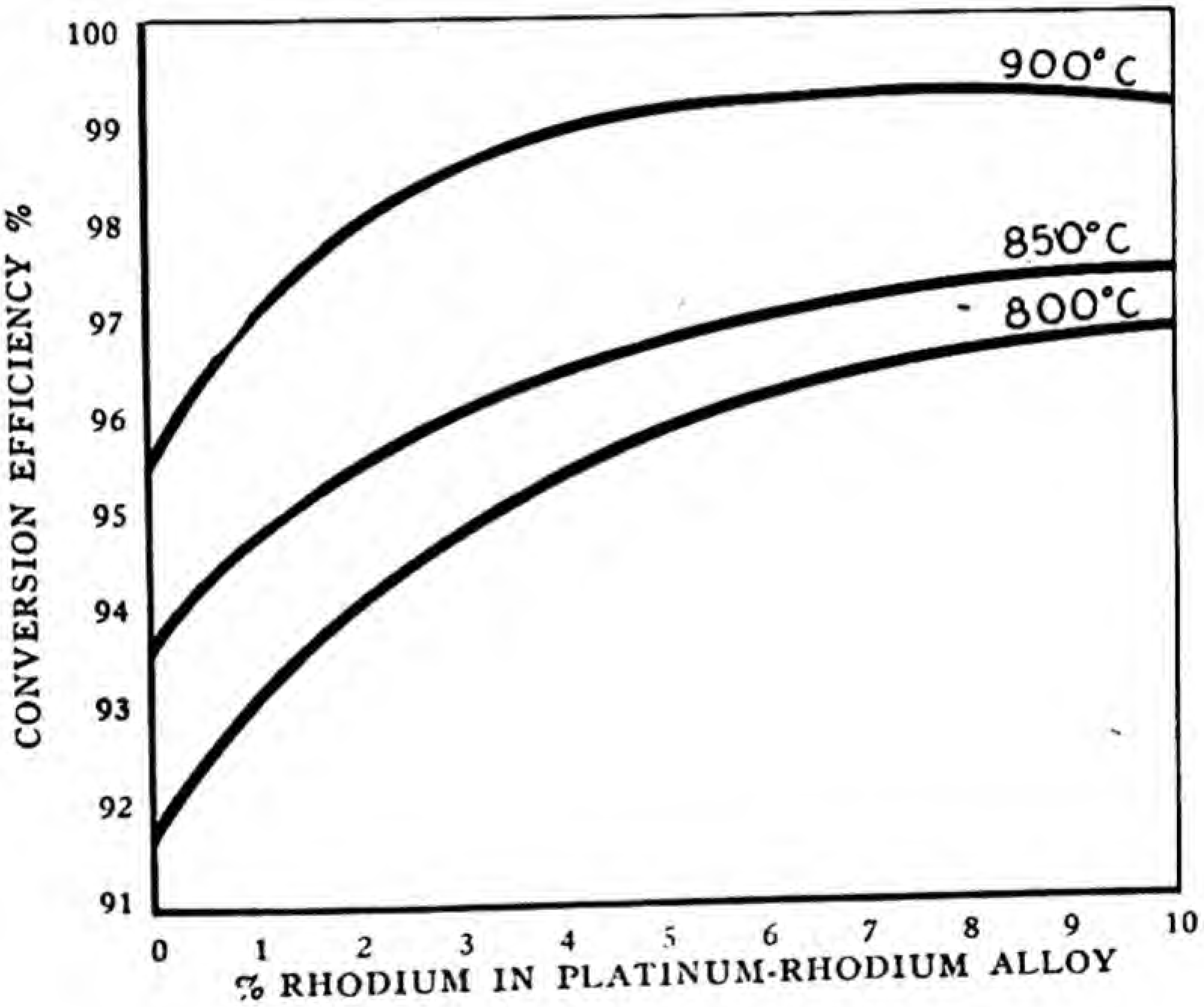

FIGURE 14

CONVERSION EFFICIENCY OF PLATINUM-RHODIUM ALLOYS

Gauze: 0.003" Diameter Wire (0.076 mm), 80 Mesh (1024 per sq. cm).
Rate: 100 lb NH_3 per Troy Ounce of Catalyst per 24 Hours.
(Courtesy of Baker & Co., Inc., Newark, N. J.)

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[162] Davis: U. S. Patent, 1,706,055 (1929).
[162a] Tilley and Whitehead: U. S. Patent 2,004,141 (1935).
[164] *Platinum-Rhodium Gauze, D-B 750.* Baker & Co., Inc., Newark, N. J.

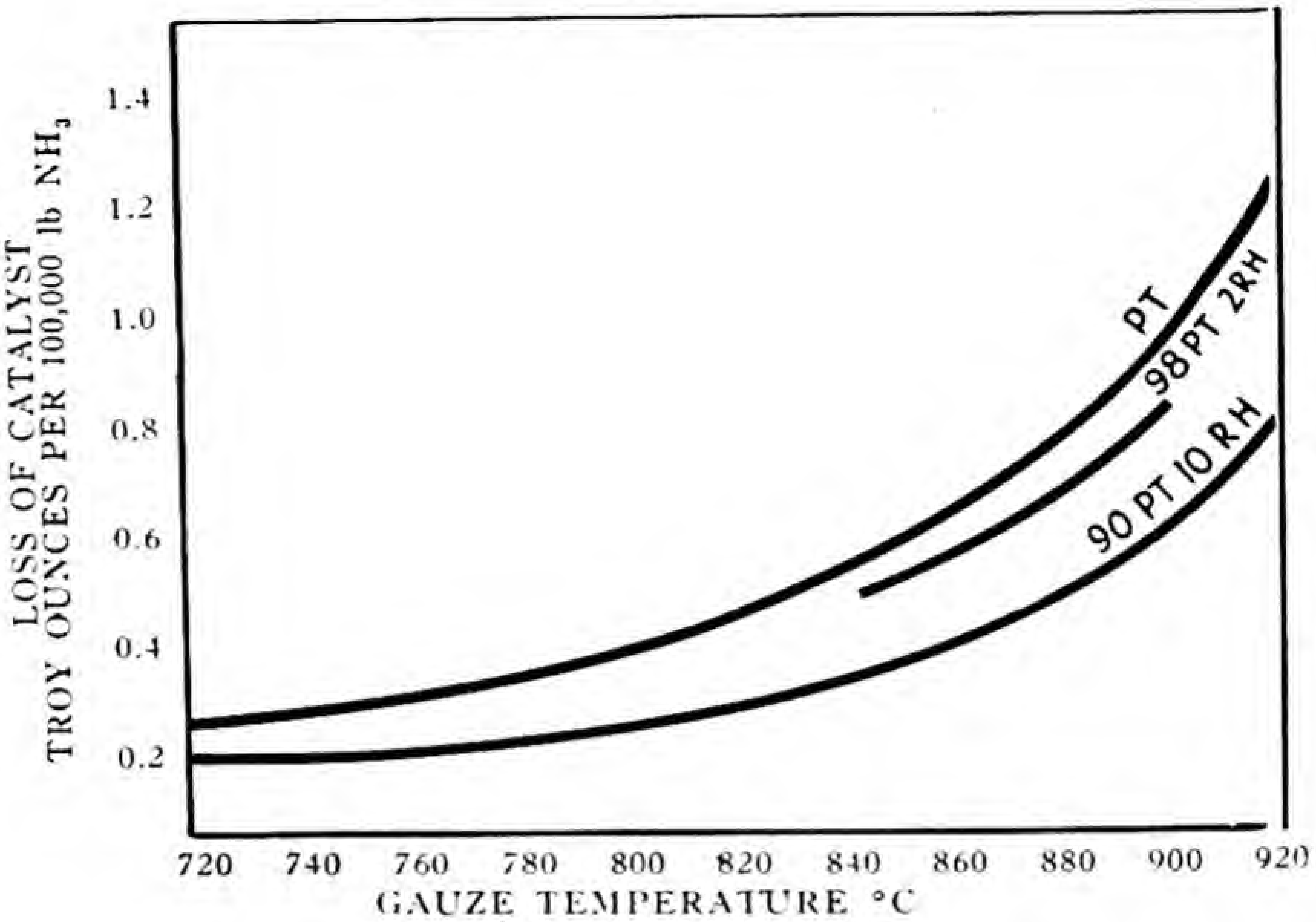

FIGURE 15

LOSS OF CATALYST
Gauze: 0.003" Diameter Wire (0.076 mm), 80 Mesh (1024 per sq. cm).
Rate: 100 lb NH_3 per Troy Ounce of Catalyst per 24 Hours.
NH_3: 10.5—11.0% by Volume.
(Courtesy of Baker & Co., Inc., Newark, N. J.)

This new platinum-rhodium catalyst is used in all the ammonia oxidation plants of the du Pont Company.[159]

The publications, dealing with platinum catalysts, are numerous, but only a few can be mentioned here. Platinum may be prepared for catalytic purposes (1) as platinum sponge, which is obtained by thermal decomposition of ammonium chloroplatinate; (2) as platinum black obtained by wet reduction of platinum salts; and (3) as colloidal platinum obtained by wet-reduction methods yielding platinum sols of high dispersion. The black and colloidal forms usually are the most active catalysts.

The particle sizes of different platinum preparations are as follows:[174]

Method of preparation	Particle size, Å
Cathodic dispersion in hydrogen	41 ±5
Active platinum from platinum oxide	46

Method of preparation	Particle size, Å
Platinum black:	
From Heraeus Company	69.3
Precipitated from acid solution of $PtCl_6$ by Al	52.8
Precipitated from neutral solution of 5% $PtCl_6$ by granular Al	48.0
Platinum sponge: Obtained by heating $(NH_4)_2PtCl_6$ at 250 and 320°C respectively	90 and 112.7

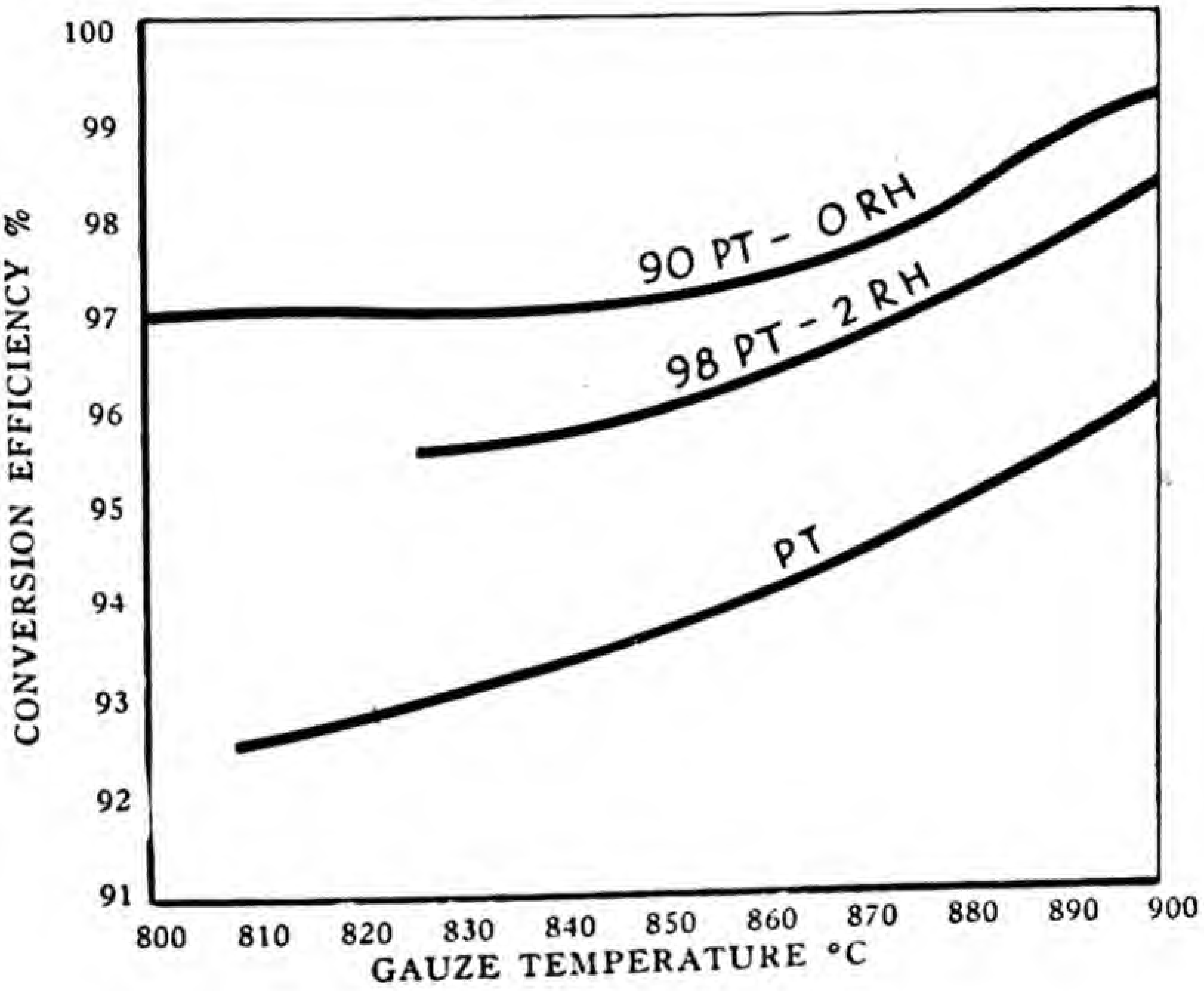

FIGURE 16

CONVERSION EFFICIENCY OF PT AND PT-RH CATALYSTS AT VARIOUS GAUZE TEMPERATURES
Gauze: 0.003″ Diameter Wire (0.076 mm), 80 Mesh (1024 per sq. cm).
Rate: 100 lb NH_3 per Troy Ounce of Catalyst per 24 Hours.
(Courtesy of Baker & Co., Inc., Newark, N. J.)

Platinum black is prepared by reduction of chloroplatinic acid, H_2PtCl_6, in alkaline solution with formaldehyde, sodium formate, glycerin, glucose, hydrazine hydrate, etc.[165, 166] Very active col-

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[165] Feulgen: *Ber.*, **54**, 360 (1921).
[166] Loew: *Ber.*, **23**, 289 (1890).

loidal platinum and palladium catalysts were prepared by Paal[167] and Skita.[177] Colloidal metals provide for excellent catalytic activity, but such catalysts are often difficult to separate from the conversion products in conversions on large scale. The preparation of colloidal metals has been extensively discussed by Svedberg.[168]

A very active form of catalytic platinum is obtained by precipitating the platinum chloride as hydrated platinum oxide, washing, and reducing with hydrogen at atmospheric pressure in a suspension in water, alcohol, acetic acid or other media.

The platinum oxide, PtO_2, known as Adams Catalyst is an important reduction and oxidation catalyst, and is prepared as follows:[169, 170, 171, 172, 172a]

In a porcelain casserole or a Pyrex beaker 3.5 g of commercial chloroplatinic acid, 10 cc water, and 35 g of sodium nitrate (C.P.) are evaporated to dryness by heating gently over a Bunsen flame while stirring with a glass rod.

The temperature is then raised at a rate at which 350–370°C is reached within about ten minutes. The mass fuses, and brown fumes of nitrogen oxides are evolved. A precipitate of brown platinum oxide separates. The reaction mechanism is approximately as follows:

$$H_2PtCl_6 + 6NaNO_3 \rightarrow Pt(NO_3)_4 + 6NaCl + 2HNO_3$$

$$Pt(NO_3)_4 \rightarrow PtO_2 + 4NO_2 + O_2$$

$$PtO_2 + H_2O \rightarrow PtO_2 \cdot H_2O$$

If foaming occurs, the mass must be stirred vigorously and an additional flame directed at the top of the reaction mixture. If the burner under the casserole is removed when foaming starts, the top of the fused mass solidifies and the foaming may become sufficient to carry material over the sides of the container.

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[167] Paal et al.: *Ber.*, **35**, 2195 (1902); *ibid.*, **37**, 126 (1904); *ibid.*, **38**, 1398 (1905); *ibid.*, **40**, 2201, 2209 (1907); *ibid.*, **49**, 548 (1916); *ibid.*, **50**, 722 (1917).

[168] Svedberg: *Die Methoden zur Herstellung kolloidaler Lösungen anorganischer Stoffe*, Dresden, Theodor Steinkopff, 1909.

[169] Adams and Shriner: *J. Am. Chem. Soc.*, **45**, 2171 (1923).

[170] Adams, Vorhees and Shriner: *Organic Syntheses, Vol. 8*,. New York, John Wiley & Sons, Inc., 1928.

[171] Carothers and Adams: *J. Am. Chem. Soc.*, **45**, 1071 (1923).

[172] Vorhees and Adams: *J. Am. Chem. Soc.*, **54**, 1397 (1932).

[172a] Short: *J. Soc. Chem. Ind.*, p. 14T (1936).

In about 15 minutes, the temperature reaches about 400°C, and the evolution of gas greatly decreases. At the end of about twenty minutes, the temperature should be 500–550°C, and at this point, there is only gentle evolution of oxides of nitrogen. The temperature is held at this point, best with the full force of the burner directly on the casserole, until about thirty minutes have elapsed, when the fusion should be complete. The mass is allowed to cool, and is then treated with 50 cc of water. The brown precipitate settles to the bottom and can be washed by decantation once or twice, then filtered on a hardened filter or in a Gooch crucible, and washed on the filter until practically free from nitrates.

If the temperature of fusion has not been high enough, or has not been maintained for a sufficiently long time, the precipitate tends to become colloidal on addition of water and does not filter well, and the yield and activity are lower. Sometimes, the precipitate becomes colloidal only when practically all of the nitrates is removed; in this case, the washing is stopped as soon as the colloid starts to form as small traces of the salt do not affect the efficiency of the catalyst.

The oxide is used directly, or more generally, it is dried in a desiccator. The yield is 1.57–1.65 g, i.e., 95–100 per cent of the theoretical amount. In order to avoid loss of activity, the oxide should be used shortly after preparation, i.e., within a few weeks at most.

The brown oxide is a heavy granular powder which has to be reduced before using as a reduction catalyst. This reduction is carried out directly in the hydrogenation vessel, and the time it takes to convert the oxide to reduced black is called the lag. This varies from several seconds to 2–3 minutes, and in media consisting of solvent plus substance to be hydrogenated sometimes 10–15 minutes.

The preparation of a platinum catalyst of this type supported on diatomite or a similar porous material has been described by Martin.[173]

The platinum metals may also be deposited in catalytically active form on surfaces of platinum metals and base metals. By cathodic dispersion in inert gases or vacuo, platinum may be deposited on glass, quartz, mica, base metals or other materials.[174] Platinum may be deposited electrolytically on nickel[175] from a phosphate solution, or on polished copper[175] at 70°C from a solution containing 13.3 g chloroplatinic acid, 45 g $(NH_4)_2HPO_4$, 240 g $Na_2HPO_4 \cdot 12H_2O$ per liter, with a current density of 0.4 amp. per square decimeter.[174] If such depositions of catalytic active metals are made on suitable surfaces, it is possible to make catalytic converters in which the dispersion of the catalyst or packing with granules is obviated, and undue losses of catalyst are prevented. Thus precious metals may be used in operations where otherwise their use would not be possible. Several methods of catalysis based on this principle have been devised by the author.[175]

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[173] Martin: U. S. Patent, 2,207,868 (1940).

[174] *Gmelins Handbuch der anorganischen Chemie*, Hydrogen; System No. 2, Platinmetallen; System Nos. (63–68); Verlag Chemie G. m. b. H., Berlin (1936).

Palladium is a catalytic metal suitable for a wide range of catalytic reactions at comparatively low operating temperatures, which, as a matter of fact, is a general characteristic of platinum metals. A list of commercially available palladium catalysts, published by Baker & Co., Inc., gives a good idea of the types and uses of this metal and its oxides as a catalyst:[176]

1. Carrier-free catalysts of high activity:
    - Palladium black
    - Palladium oxide

2. Catalysts for reactions in the gaseous phase:
    - Palladium asbestos, 5 or 10 per cent
    - Palladium charcoal, 8–14 mesh, 0.5 or 1 per cent
    - Palladium silica gel, 0.3 per cent
    - Palladium on Alfrax, 0.5 per cent
    - Palladium on alumina pellets, 0.5 per cent
    - Palladium on Pyrex glass fibre, 5 per cent

3. Catalysts for reactions in the liquid phase, especially for hydrogenation at room temperature and atmospheric pressure:
    - Palladium on activated charcoal powder, 5 or 10 per cent
    - Palladium on alumina powder, 5 per cent
    - Palladium on calcium carbonate, 5 per cent
    - Palladium on zinc carbonate, 5 per cent
    - Baker Colloid 46 (0.5 gram Pd per liter)
    - Palladium gelatin colloid, 3 per cent solution

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[175] Lohse: *Unpublished Data;* Can. Pat. 403,743 (1942).

[176] *Bibliography of Patents on Palladium as a Catalyst. Part 1,* United States and German Patents, Newark, N. J., Baker & Co., Inc., 1939.

Much of what has been said about the preparation of platinum catalysts applies to the preparation of palladium catalysts. For preparation of colloidal palladium according to Paal's method,[167] the sodium salt of protalbinic acid is used instead of the sodium salt of lysalbinic acid, since only the former gives stable solutions. Skita [177] also prepared colloidal palladium solutions similarly to those of platinum.

Palladium has the property of adsorbing a very large quantity of hydrogen, viz., about 900 volumes to 1 volume of palladium. As a matter of fact, palladium is an excellent hydrogenation catalyst, which may be ascribed to the ability of the metal to readily form labile combinations with hydrogen. An interesting application of the catalytic properties of palladium is found in cigar and cigarette lighters and gas igniters.[176]

Ruthenium and its compounds are exceptionally good oxidation catalysts and are as such superior to most other oxidation catalysts.[178] As a catalyst for the reduction of CO_2, ruthenium is superior to any other contact. CO_2 is converted to methane at 100°C. If the ruthenium is alkalized with K_2CO_3 or Rb_2CO_3, methane and higher gaseous and liquid hydrocarbons are formed. The weaker alkalies do not give higher hydrocarbons.[179]

Osmium tetroxide, OsO_4, is also a very good oxidation catalyst. It is obtained as glistening transparent needles by burning metallic osmium, or by oxidation of the lower oxides. The fumes of this oxide are very poisonous, and attack the skin, the eyes, and the lungs.[178]

Rhodium, in the dispersed state, is a useful catalyst for hydrogenation, dehydrogenation and oxidation. Its most extensive catalytic use is as a high-temperature oxidation catalyst when alloyed with platinum.

Many iridium salts have catalytic properties. Thus the presence of a trace of iridium chloride catalyzes the reduction by oxalic acid of tetravalent platinum tō the divalent stage.[180]

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[177] Skita: *Ber.*, **42**, 1627 (1909); *ibid.*, **45**, 3585 (1912).

[178] Hoffman et al.: *Ber.*, **45**, 3329 (1913); *ibid.*, **46**, 1657 (1913).

[179] Fischer, Bahr and Mensel: *Brennstoff-Chem.*, **16**, 466 (1935).

[180] *Salts of the Platinum Metals and Gold*, Newark, N. J., Baker & Co., Inc., 1940.

Mixed Catalysts

Mixed catalysts are defined by Mittasch[138, 181] as mixtures of two or more substances which are used as catalysts instead of a single substance. Actually, the majority of catalysts are mixed catalysts. Mixed catalysts were thoroughly studied in connection with ammonia and Fischer and Tropsch synthesis[22] with excellent results. In studies on fixation of nitrogen by different metals, Mittasch found that the fixing of nitrogen increases in the presence of certain foreign substances, e.g., metallic silicon, heated for a few hours at 1000°C, gave a product containing two per cent nitrogen as nitride, but by making the following additions, the fixation attained the following magnitudes in per cent:

Na-K-carbonate	NaF	$CaCO_3$	$BaCl_2$	
9.5	20.4	19.0	19.7	% N
			(theor. 40%)	

It was then concluded that the formation of ammonia is probably analogous to the formation of nitrides, and on this working hypothesis, a series of mixed iron catalysts was developed with successful results (see page 102). Considering the fact that intermediary nitride formation has later been established in the catalytic synthesis of ammonia, this hypothesis was very ingenious indeed. As judged by figure 5, page 50, and the following figure 17, there is an optimum composition of the mixed catalysts for optimum efficiency of catalytic synthesis of ammonia.

For alloys or intermetallic compounds, it is probable that the further apart two metals stand in the electrochemical series, the higher is the catalytic activity of their alloy.[182]

Ipatieff[163] studied the problem of mixed catalysts in hydrogenation reactions. In the case of hydrogenation of terpenes in contact with a mixture of nickel oxide and alumina under hydro-

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[181] Mittasch, A.: *Einiges über Mehrstoffkatalysatoren*, 35th Meeting of the German Bunsen Soc. for Applied Physical Chemistry, Spektroskopy and Atomic Structure, Berlin, Verlag Chemie, 1930.

[182] Berkman, S., J. C. Morrell, and Gustav Egloff: *Catalysis, Inorganic and Organic*, New York, Reinhold Publishing Corp., 1940.

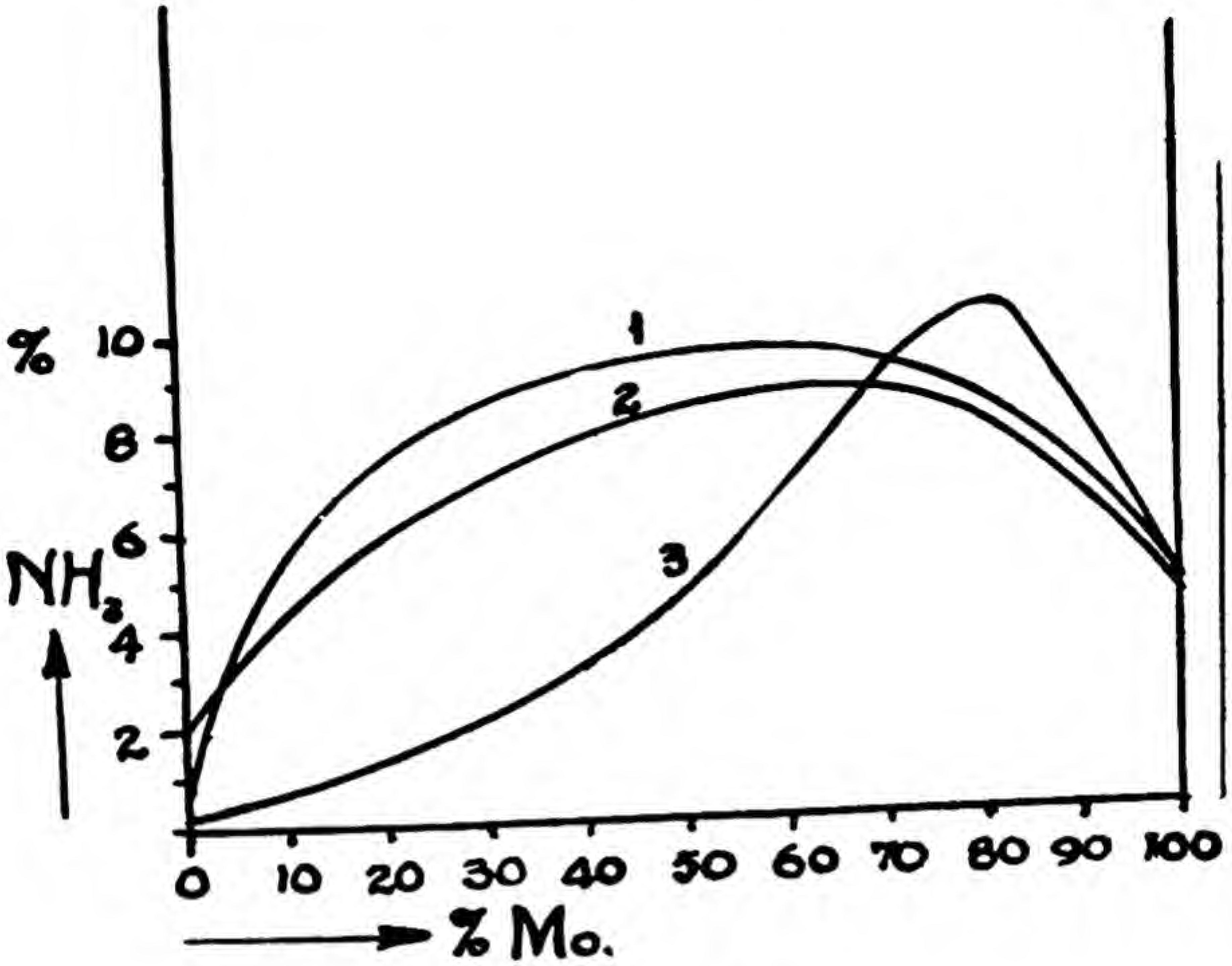

FIGURE 17

MIXED MOLYBDENUM CATALYSTS
Catalytic action of Mo—Co (1), Mo—Fe (2), and Mo—Ni (3) in ammonia synthesis (Mittasch).

gen pressure, at 200°C, the reaction is considered to proceed in three steps:

(1) Reduction in the presence of the nickel oxide;
(2) Dehydration in the presence of the alumina to give an olefin;
(3) Hydrogenation of the olefin.

The reaction scheme is:

1. $C_{10}H_{16}O + H_2 \rightarrow C_{10}H_{18}O$
2. $C_{10}H_{18}O \rightarrow C_{10}H_{16} + H_2O$
3. $C_{10}H_{16} + H_2 \rightarrow C_{10}H_{18}$

Ipatieff assumes that in the joint action of catalysts, a labile complex is formed between the two catalysts, i.e., nickel oxide and aluminum oxide, and that this complex decomposes and reforms in statu nascendi. The reformed catalyst is considered to be more active, so that the reaction proceeds at a much lower temperature. Many experiments are reported by Ipatieff.[74]

Mixed catalysts may also be made on surfaces of a converter by electrodeposition of metals, care being taken that the deposit should give a rough and preferably spongy surface. This may also be attained by making an amalgam on the surface of a metal or an alloy and then removing the mercury by means of heat or by chemical treatment. Alloys, consisting of a plurality of metals, may be made so as to include a component which can be removed by chemical treatment thus leaving an unsaturated surface of catalytic activity. Such removable components are alkali metals, alkaline earth metals, aluminum, silicon, zinc, lead, etc.[45]

Attention should also be called to the studies of Reinacker et al.[183] on the catalytic activities of alloys, and to the study of mixed heteropolyacid catalysts for oxidation of naphthalene by Brown and Fraser.[184]

Hopcalite catalysts [185] were the result of studies on removal of carbon monoxide from air at ordinary temperature during World War I. A brief summary of the very interesting and important observations will be given here.

Silver oxide and sodium peroxide, in alternating layers, absorbed about 98 per cent carbon monoxide passed through at room temperature. The reaction starts rapidly when the mass is heated to 40–50°C and then proceeds on its own heat of reaction. Probably, the silver oxide oxidizes the carbon monoxide to carbon dioxide which forms sodium carbonate with the sodium peroxide. Small amounts of moisture are beneficial for this reaction.

Finely divided manganese dioxide, MnO_2, was prepared by various methods. With dry gas (CO) the action of equal parts of manganese dioxide and silver oxide was catalytic, the CO being continuously oxidized by the oxygen in the air.

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[183] Reinacker et al.: *Z. anorg. Chem.*, **242**, 302 (1939); *J. prak. Chem.*, **158**, 95 (1941); *Chem. Abstracts*, **36**, 380 (1942); *Z. Elektrochem.*, **47**, 805 (1942).

[184] Brown and Fraser: *J. Am. Chem. Soc.*, **69**, 2917 (1942).

[185] Lamb, Bray and Fraser: *Ind. Eng. Chem.*, **12**, 213 (1920).

It was also found that an equally active catalyst can be made from cobalt oxide, MnO_2, and silver oxide in the proportion 20:34:46, this mixture being prepared by the interaction of silver permanganate and moist cobalt oxide. With dry gas, the life of this catalyst is very long, but moisture destroys the activity, although it is revived rather quickly when the catalyst is treated again with the dry gas.

It is found that the amount of water of hydration, left in the prepared oxide, is a determining factor in the preparation of active catalysts. The oxides are granulated, the granules being very porous, and the action at low temperatures is believed to be dependent on the large surface exposed to the oxygen in the air and the CO. 100 cc of 14–16 mesh granules of one sample are found to contain only 8.8 cc solid material, whereas the space between the granules is about 47 cc, leaving a capillary volume of about 44 cc. The high porosity is considered responsible for the poisoning effect of water at room temperature, an effect which decreases at higher temperatures.

The best catalysts contained active MnO_2 as the chief constituent, the composition of Hopcalite I being: 50% MnO_2, 30% CuO, 15% Co_2O_3 and 5% Ag_2O. This material acts as a catalyst at 0° with as low a concentration of CO as 0.2% dry gas.

The physical chemistry of these catalysts has been studied recently,[186] and it was found that the active catalysts, with one exception, consist of crystallites so small that in classical language they would be called amorphous. Samples of identical compositions and different patterns are not necessarily identical in catalytic behavior.

Carriers

In a great number of cases, where finely dispersed catalysts are used, it is often advantageous to deposit the finely dispersed catalyst on a carrier material. The action of such materials is often more than just a physical one. Besides the advantage of easier separation when carriers are used, the carrier undoubtedly prevents recrystallization of the catalyst during use, especially at high temperatures, this also being true of the prevention of sintering under the same circumstances. The carrier undoubtedly influences the adsorption of the reactants considerably and, for that matter, also the desorption of the reaction products. In cases of poisoning, the choice of a suitable carrier may considerably offset the poisoning effect. One thing seems to be certain when preparing carriers from natural materials, such as diatomaceous earth, pumice, clays, porcelain, gypsum, cement, and similar products, and that is the necessity of removal of soluble substances which may readily react with the catalyst to be deposited.

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[186] Pitzer and Fraser: *J. Phys. Chem.*, **45**, 761 (1941).

Very good carriers can be made from synthetic zeolites, the chemical and physical conditions of which can be controlled. Zeolites have been extensively studied by Jaeger and Bertsch,[187] who developed a considerable number of catalysts on this basis, two examples of which are as follows:

Example I: (U. S. Patent 1,701,075)

(1) 25 mol of vanadic acid are acidified with sulphuric acid and reduced with alcohol at an elevated temperature until a clear blue solution is formed. Instead of alcohol, other reducing agents, such as oxalic acid, citric acid, tartaric acid, sugar, formaldehyde, hydroxylamine, hydrogen, nitrous acid, and the like, may be used. The excess of reducing agent is removed, as far as possible, by boiling the warm solution, and alkali metal carbonate is added. Vanadyl hydroxide precipitates out and can be washed with water until there is no test for SO_4. The washed precipitate is then treated with sufficient alkali metal hydroxide to dissolve it in the form of a dark-brown solution.

(2) 1.75 mol of copper carbonate are treated with sufficient aqueous ammonia solution to form the deep blue cuprammonium carbonate.

(3) 10 mol of SiO_2, in the form of sodium or potassium silicate solution, are diluted with 10 volumes of water and made slightly

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[187] Jaeger and Bertsch: U. S. Patents, 1,701,075 (1929), 1,782,353 (1930), and 1,840,450 (1932).

ammoniacal. Pumice meal, kieselguhr, or asbestos fibers, or their mixtures are stirred into the solution until the mixture remains just stirrable.

Solution (2) is poured into suspension (3) with good agitation, warmed up to 65°C, and solution (1) added rapidly with further stirring. Formic or acetic acid is cautiously added until the liquid is just neutral to litmus. A copper-vanadyl zeolite precipitates out and is thoroughly washed and dried. An enhanced mechanical strength can be obtained by adding a little water glass to the wash water.

After drying, the mass is broken into fragments and possesses excellent base-exchange power. The product is also a good reduction or oxidation catalyst. When used for reductions, the catalyst receives a preliminary treatment with hydrogen at 250–350°C and is then ready for use. Nitrobenzene is reduced in a stream of hydrogen to give good yields of aniline, using the above catalysts. In a similar manner, crotonaldehyde is reduced to normal butyl alcohol. Aluminum or thorium can also be introduced by base exchange by using solutions of their nitrates, and the substitution results in a still better reduction catalyst.

When the product is to be used as an oxidation catalyst, a preliminary treatment, at 400–500°C, with acid vapors and air is advantageous. The catalyst thus prepared oxidizes methane to formaldehyde, methyl alcohol, and formic acid and is also useful in oxidizing methyl alcohol to formaldehyde and naphthalene to naphthaquinone and phthalic anhydride. The oxidizing effect can be still further improved by introducing silver or vanadium by base exchange, using, for example, a silver sulfate or a vanadium chloride solution.

Example II: (U. S. Patent 1,840,450, 1932)

(1) 165–200 parts kieselguhr are impregnated with a concentrated solution of chromic acid and are reduced in a stream of hydrogen at 300°C.

(2) 1 mol of zinc, in the form of zinc nitrate, is dissolved to form potassium zincate using a minimum of caustic potash, and 0.25 mol of lead nitrate is similarly dissolved in caustic potash in the form of potassium plumbite and is mixed with the zincate solution.

(3) 4.5 mols of water glass are stirred with 10% by weight of cadmium chromate and mixed with the kieselguhr mixture, (1), to form a suspension.

The mixed solutions (2) are stirred into the suspension (3) with gentle warming and if necessary, dilute nitric acid is added to accelerate the formation of a gel. The gelatinous precipitate, which comes down, is a potassium-zinc-lead-zeolite in which the kieselguhr impregnated with chromium and the cadmium chromate are embodied in a very fine state of division. The precipitate is pressed, dried, and a solution of equal parts of cerium nitrate and manganese nitrate is permitted to trickle over it at an elevated temperature in order to exchange the alkali metal of the zeolite for a mixture of cerium and manganese, the treatment being carried on until the base exchange is as complete as possible. The product is then impregnated with an amount of ammonium vanadate solution corresponding to the cerium and manganese introduced in order to form a salt-like combination with the cerium and manganese of the zeolite.

The product described above is treated with a mixture of CO and hydrogen at 300–400°C at high pressure, and after the catalyst is reduced, rapid formation of methyl alcohol sets in. If the base exchange and the subsequent treatment with the vanadate are omitted, the catalyst, when subjected to the action of a carbon monoxide-hydrogen mixture at 300–400°C, yields higher alcohols and ketones in addition to liquid reaction products containing methyl alcohol, particularly when the gas is very rich in CO.

It appears to be important to choose a carrier that does not react too intimately with the catalyst deposited on it under the reaction conditions, since otherwise, the catalyst becomes deactivated too fast. Consequently, where carriers are used at higher temperatures, refractory oxides are, generally, very suitable. An example of this is the oxide of magnesium which, for many purposes, constitutes an excellent carrier material.

A detailed bibliography, on the nature of carrier materials and their properties, has been discussed by Berkman, Morrell, and Egloff,[182] and they summarize methods for the deposition of catalysts on carriers as follows:

I. Surface deposition:
   (1) Precipitation of the catalyst on the carrier
   (2) Electroplating the catalyst on the carrier
   (3) Coating the carrier with a paste
   (4) Deposition of colloidal metals in which a spreading of the reduced metal, in nascent state, takes place

II. Internal deposition (uniform distribution of the catalyst throughout the carrier, the internal surface of the carrier being coated):

(1) Permeating or impregnating porous supports with a salt solution
(2) Simultaneous precipitation of oxides

Groll and Roberts[76] studied the use of activated alumina as a carrier. For this purpose, the alumina is impregnated with a solution of the desired catalytic compound, the procedure being as follows: The alumina is heated under reduced pressure to 200°C to expel the adsorbed air, after which it is covered with the impregnating solution and then cooled before releasing the vacuum. The impregnation can also be accomplished by letting the carrier stand for some time submerged in the solution at room or elevated temperatures.

Activated alumina also improves, in many cases, the dehydrogenation catalyst which it supports. Thus, chromium oxide, in the form of an active gel, is a selective dehydrogenation catalyst at about 400°C, giving conversions approximating equilibrium conditions, although these conversions are low because the equilibrium, at such a low temperature, does not favor the formation of olefin, and it would, therefore, be better to operate at higher temperatures. However, chromium oxide is unstable at 500°C or higher. Activated alumina is stable above 500°C and constitutes, therefore, a very suitable carrier for chromium oxide.

Activated alumina, as a carrier, may also be used to modify the activity of catalysts whose action is too drastic. An example of this is contact materials which are so active that they cause splitting of the carbon to carbon bond in hydrocarbons. Thus, reduced nickel oxide on pumice is very active but causes complete cracking to carbon and hydrogen at a temperature as low as 450°C, whereas nickel on activated alumina gives favorable conversions and ratios in dehydrogenation. Similarly, iron oxide, when prepared as an active gel, favors disruption of the hydrocarbon molecule, but it is a selective dehydrogenation catalyst when supported on active alumina.

The influence of the carrier, on the catalytic properties of the contact mass, has been very well demonstrated by Vernon and

Brown,[188] who studied the vapor-phase esterification of benzoic acid with ethyl alcohol, using silicon carbide or alundum as carriers for a series of oxide catalysts studied. The data for this conversion, at the optimum temperature for each catalyst, and the percentage conversions at three different space velocities, are as follows:

Oxide	Optimum temp., °C	Space velocity of acid	Conversion of acid to ester, %	Conversion of acid by side reactions, %
(1) Silicon carbide:				
ZrO_2	450	304	18	3
		152	20	3
		76	31	11
ZnO	450	304	11	4
		152	12	5
		76	17	7
MgO	450	304	74	. .
		152	82	. .
		76	86	. .
Al_2O_3	430	295	49	5
		148	51	9
		74	58	22
Cr_2O_3	450	304	21	. .
		152	23	4
		76	26	7
CaO	390	278	16	32
		139	23	17
		70	37	18
BaO	450	304	23	17
		152	29	19
		76	43	31
SrO	450	304	17	9
		152	24	10
		76	46	12
BeO	410	286	5	4
		143	8	10
		72	14	10
Mn_3O_4	410	287	79	9
		143	75	16
		72	74	19
TiO_2	390	278	28	2
		139	36	. .
		70	49	2
WO_3	390	282	3	9
		141	4	12
		70	5	12

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[188] Vernon and Brown: *Ind. Eng. Chem.*, **32**, 534 (1940).

Oxide	Optimum temp., °C	Space velocity of acid	Conversion of acid to ester, %	Conversion of acid by side reactions, %
(2) Alundum:				
ZrO_2	430	292	75	12
		146	75	15
		73	76	15
ZnO	430	290	8	6
		145	11	4
		72	13	26
MgO	430	292	73	5
		146	77	5
		73	78	7
Al_2O_3	410	282	74	17
		141	81	12
		70	81	13
Cr_2O_3	450	298	5	3
		149	9	9
		75	13	9
CaO	390	274	10	42
		137	19	39
		68	24	41
BaO	450	298	28	15
		149	34	21
		75	42	38
SrO	410	282	7	29
		141	12	28
		71	24	27
BeO	450	298	2	12
		149	4	13
		75	13	43
Mn_3O_4	390	278	82	11
		139	83	11
		70	83	11
TiO_2	370	270	98	..
		135	97	..
		68	88	3
WO_3	390	282	0	10
		141	2	12
		71	5	21

Of newer promising developments should be mentioned aerogels which yield supported catalysts of low apparent density,[188a] and catalysts supported on synthetic organic high-polymers.

Activated clays are used in cracking of petroleum, some of these clays having distinct catalytic activity, and it is reported that up to the present time, the majority of such catalysts, sold for commercial cracking, has been of the type of activated montmorillonite. This clay-silicate is a non-swelling bentonite of the ideal formula $Al_2Si_4O_{10}(OH)_2H_2O$. The structure is crystalline. In nature, every sixth aluminum ion is supplanted by a magnesium ion; this replacement of a trivalent cation with a divalent one causes deficiency in the positive charge, the lattice is, consequently, negatively charged marking this clay capable of base-exchange. Fig. 18 shows a crystal of magnesium-substituted montmorillonite.[188b]

[188a] Kistler and al.: *Ind. Eng. Chem.*, **26**, 388, 1014 (1934); *J. Am. Chem. Soc.*, **65**, 1909 (1943); *J. Phys. Chem.*, **36**, 52 (1932).

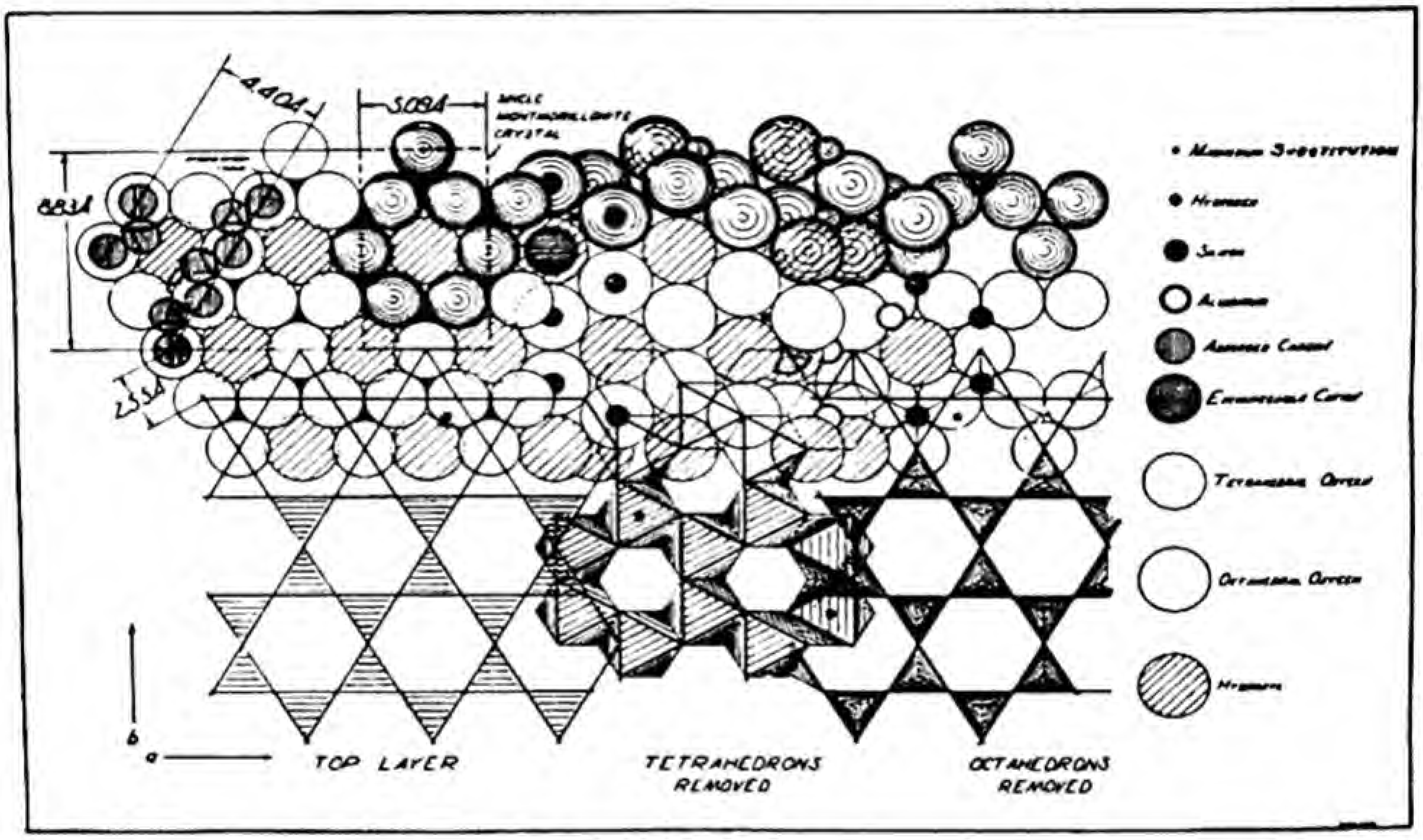
4.40Å
5.08Å
SINGLE MONTMORILLONITE CRYSTAL
8.83Å
2.55Å
Magnesium Substitution
Hydrogen
Silicon
Aluminum
Adsorbed Cation
Exchangeable Cation
Tetrahedral Oxygen
Octahedral Oxygen
Hydroxyl
b
a
TOP LAYER
TETRAHEDRONS REMOVED
OCTAHEDRONS REMOVED

FIGURE 18

Theoretical Magnesium-Substituted Montmorillonite cut away to show the successive ionic sheets composing the crystal layers. (Courtesy of Filtrol Corporation, Los Angeles, Cal.)

A recent development is the Thermofor Catalytic Cracking (TCC) Synthetic Bead Catalyst[189] for use in manufacturing aviation gasoline, which has been developed to take the place of the clay catalyst formerly used. The synthetic bead catalyst is in the form of small translucent, porous beads of extraordinary hardness (average crushing load 200 lb against 30 lb for a synthetic clay pellet), which are so rugged that they effectively resist loss by attrition. It is expected that they will have a year of commercial life (April, 1943). The increase of yield of aviation gasoline base stock is from 13 to 30 per cent, corresponding to an increase in power output of 23 to 35 per cent. This catalyst is also usable in the Houdry process for cracking gasoline. It was developed by the Socony-Vacuum Oil Company. The following figure gives a comparison of the synthetic bead catalyst pellets with natural and synthetic clay catalysts.

[188b] Davidson, Ewing and Shute: *Nat. Petroleum News*, July 7, 1943 (Reprint).

[189] Socony-Vacuum News, April, 1943, p. 8.

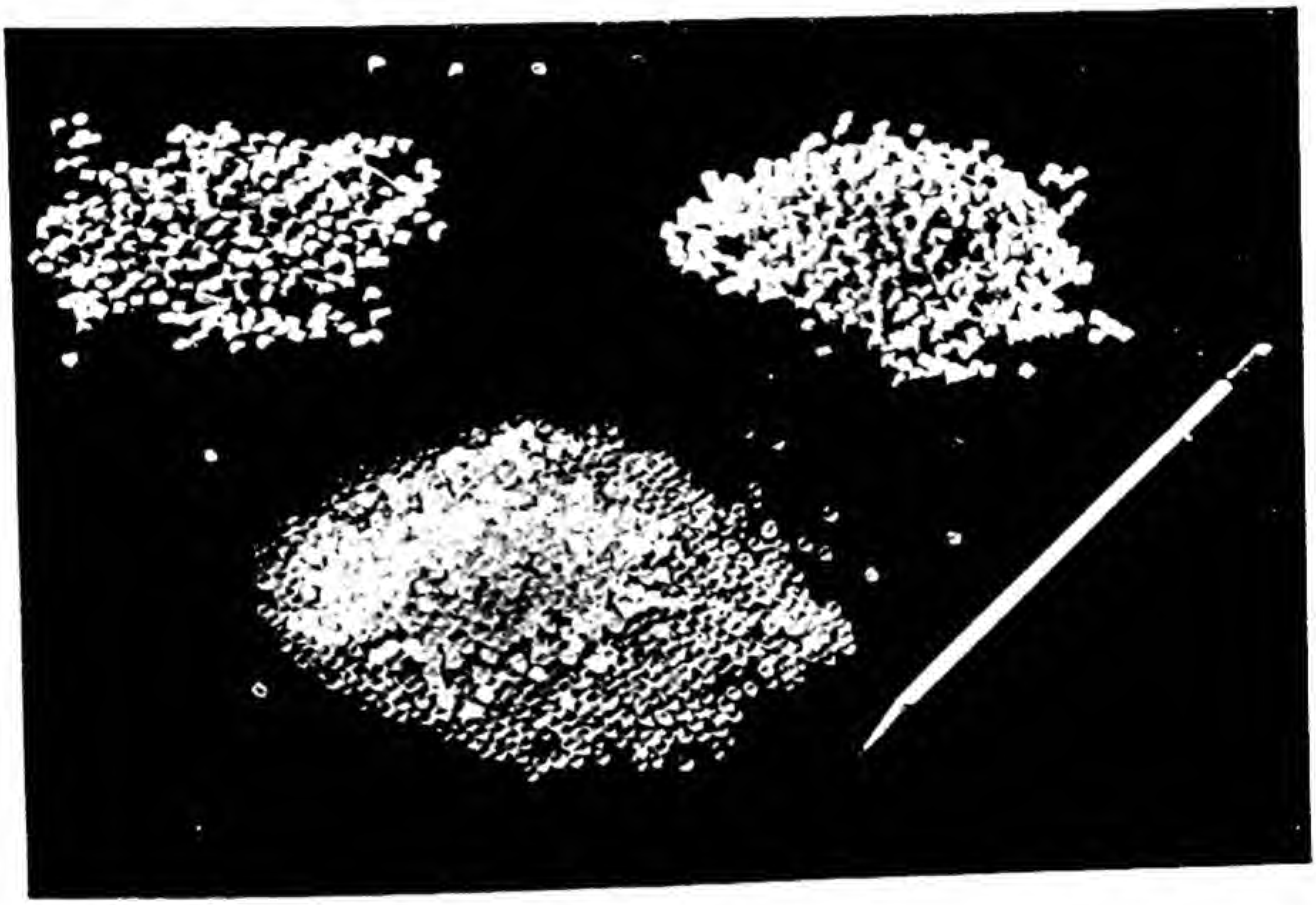

FIGURE 19

TCC SYNTHETIC BEAD CATALYST

In the upper left corner are the pellets of a natural clay catalyst, at the right are synthetic clay pellets, and in the foreground synthetic TCC beads. The pencil is included for comparing the size of the beads. (Courtesy of Socony-Vacuum Oil Company, New York, N. Y.)

Another catalyst carrier is made from bauxite and sold under the name of "Isocel."[100] Impregnated with aluminum chloride it is claimed that it produces a smoothly running isomerization reaction, and controls or entirely eliminates the reactor corrosion which is often experienced when aluminum chloride is used alone or in sludge form. This impregnated catalyst can also be used in other processes where aluminum chloride is used. Fig. 20 shows the shape of the granules made by this process.

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[100] Porocel Corp., Philadelphia: *Chemical Industries*, 55, No. 1, 89 (1944).

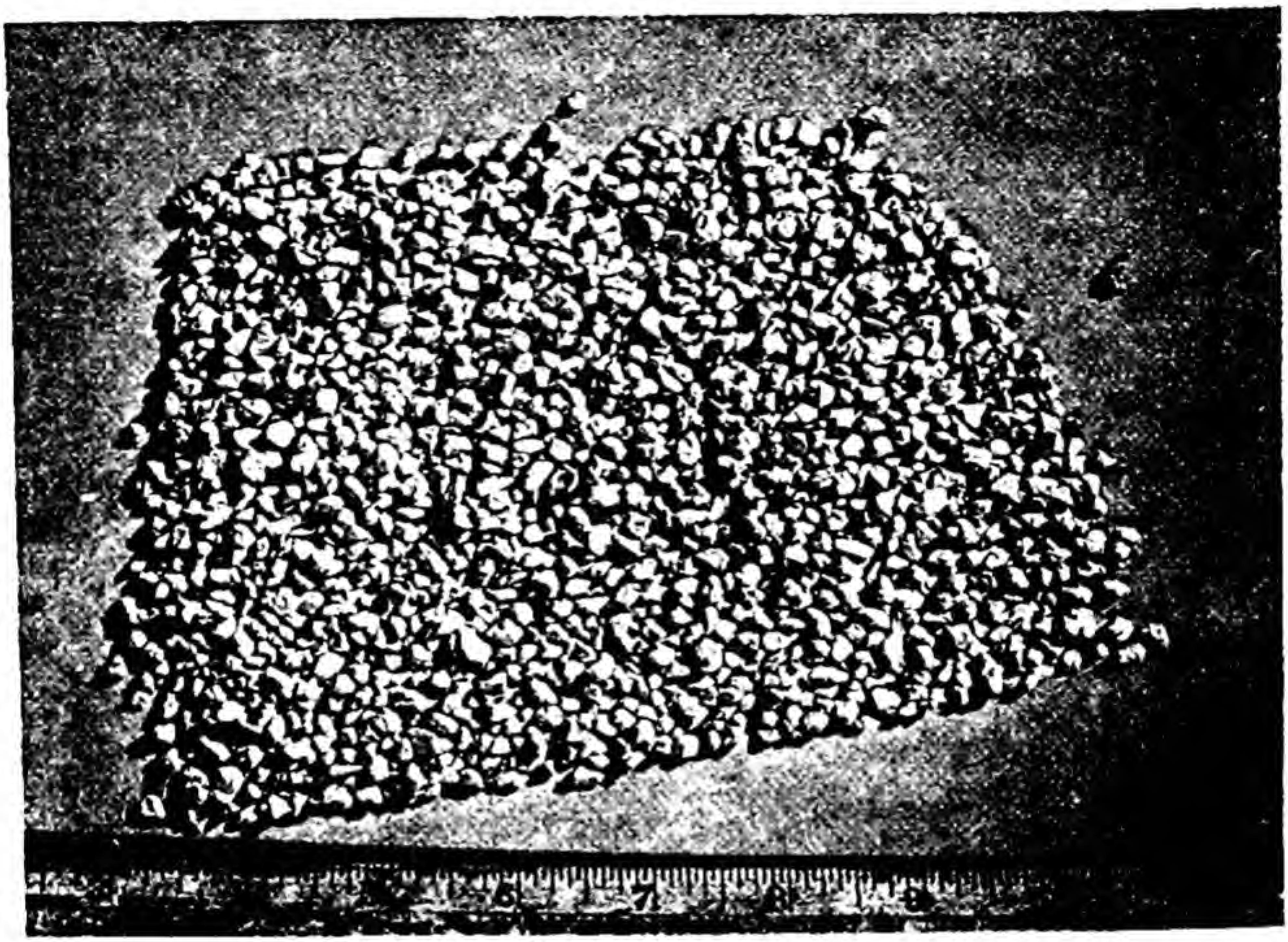

FIGURE 20

"ISOCEL" CATALYST

Bauxite carrier impregnated with aluminum chloride. (Courtesy of Attapulgus Clay Company, Philadelphia, Pa.).

GENERAL REFERENCES

Henke and Brown: *J. Phys. Chem.*, **26**, 161, 272, 324, 631 (1922); *ibid.*, **27**, 739 (1923); *ibid.*, **31**, 862 (1927) (Catalytic activity of a variety of metals); A. Farkas: *Orthohydrogen, Parahydrogen and Heavy Hydrogen.* Cambridge, Cambridge University Press, 1935; Emmett and Teller: *The Rôle of Surface Catalysis*, Twelfth Report of the Committee on Catalysis. National Research Council, New York, John Wiley & Sons, Inc., 1940, p. 68; Foster: U. S. Patent, 2,180,353 (1939); Frolich, Fenske and Quiggle: *Ind. Eng. Chem.*, **20**, 694 (1928); Grignard: *Compt. rend.*, **130**, 1322 (1900); *ibid.*, **132**, 336, 558 (1901); Hüttig and Kassler: *Z. anorg. allgem. Chem.*, **187**, 24 (1930); Ingold and Wasserman: *Trans. Faraday Soc.*, **35**, 1022, 1052 (1939); Ipatieff and Kondarev: *Ber.*, **59**, 1421 (1926); Ipatieff: U. S. Patent 2,018,065 (1935); Levi: *Atti accad. Lincei*, (6) 2, 419 (1925); Lewis: *Z. phys. Chem.*, **52**, 310 (1905);

ibid., **55**, 465 (1906); Messner and Frankenburger: *Z. phys. Chem.*, Bodenstein Festband, 1931, p. 593; Mitchell and Reid: *J. Am. Chem. Soc.*, **53**, 330 (1931); N. V. de Bataafsche Petroleum Maatschappij: German Patent, 693,707 (1940); Nyrop, J. E.: *The Catalytic Action of Surfaces*, London, Williams and Norgate, 1937; Nark, Behnke and Zobel: U. S. Patent, 1,815,790 (1931); Ott and Brugger: *Z. Elektrochem.*, **46**, 105 (1940); Rampine and Nord: *J. Am. Chem. Soc.*, **63**, 2745, 3268 (1941); *ibid.*, **65**, 429 (1943); Roginskii and Tsellinskya: *J. Phys. Chem. (U.S.S.R.)*, **13**, 1367 (1939); *Chem. Abstracts*, **35**, 373 (1941); Swann et al.: *Ind. Eng. Chem.*, **26**, 388, 1014 (1934); *ibid.*, **32**, 1607, (1940); Taylor and Kistiakowsky: *J. Am. Chem. Soc.*, **48**, 2468 (1927); Willstätter and Waldschmidt-Leitz: *Ber.*, **54**, 121 (1921).

CHAPTER IV

SPECIFIC TYPES OF CATALYTIC REACTIONS

1. Oxidation

An enormous amount of effort has been expended on catalytic oxidation reactions, many of which are of great commercial importance. The literature on this subject is vast.

There are, chemically speaking, two major types of oxidations, viz., reactions in which oxygen is added to a compound, as oxidation of an aldehyde to an acid:[1]

$$R{\cdot}CHO + \tfrac{1}{2}O_2 \rightarrow RCOOH$$

and reactions in which hydrogen is taken away from a compound, as in oxidation of an alcohol to an aldehyde:

$$R{\cdot}CH_2OH + \tfrac{1}{2}O_2 \rightarrow R{\cdot}CHO + H_2O$$

Armstrong[2] postulated that oxidation, in reality, is a process of hydroxylation which takes place under the joint influence of water and oxygen, the different stages of oxidation of methane being as follows:

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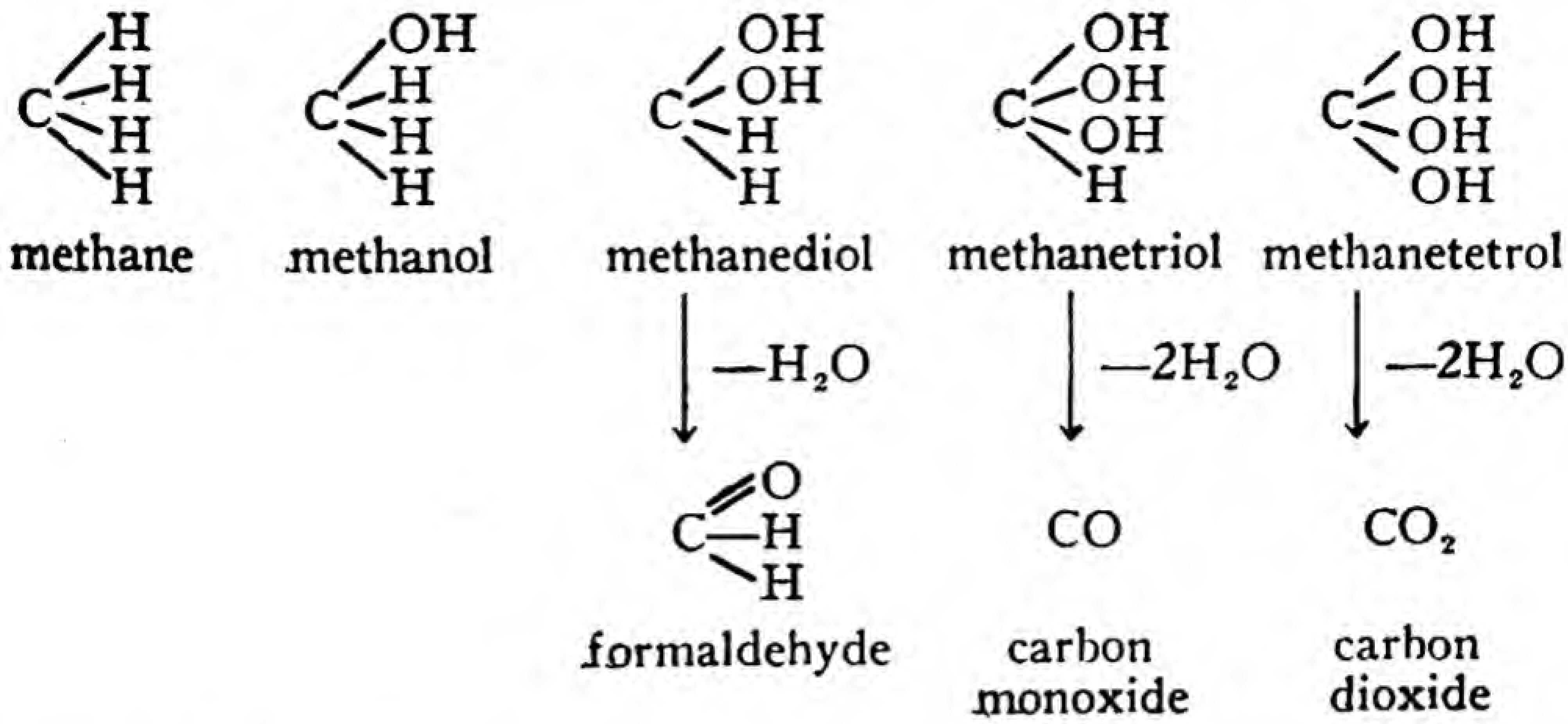
[1] Sabatier, P.: *La Catalyse en Chimie Organique*, Paris, 1920, p. 81; P. Sabatier and E. Emmett Reid: *Catalysis in Organic Chemistry*, New York, D. Van Nostrand Co., 1923.

[2] Armstrong: *Chem. Soc. Trans.*, 1088, 1903; *J. Soc. Chem. Ind.*, Jubilee Number, July, 1931, p. 182.



Oxidation mechanisms

The mechanism of oxidations depends on the oxygen carrier and the substance which is oxidized. The demarcations are probably not as sharp as any classification may make them appear, as temperature, pressure in gas and vapor reactions, and catalytic actions all are determining factors in conversions in which a substance is oxidized.

Some major types of oxidation mechanisms are, according to the observations made and the theories used for interpreting these observations, as follows:

1. Formation of intermediate compounds of higher oxidizing power than the oxidizing substance itself, e.g., ozone or intermediate peroxide formation.
2. Activation of the oxygen, atmospheric or oxygen gas.

(a) The oxygen carrier is re-oxidized, after giving off all of its activated oxygen. Such a process is true catalysis.

(b) The oxygen carrier gives off part of its oxygen, but remains oxidized and unable to become further so. Such a reaction is called induction.

3. The formation of reaction chains.
4. Dehydrogenation as suggested by Wieland.[3, 4]

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[3] Wieland, H.: *On the Mechanism of Oxidation*, New Haven, Yale University Press, 1932.

[4] Wieland: *Ber.*, **45**, 484, 685, 2608 (1912); *ibid.*, **46**, 3327 (1913); *ibid.*, **47**, 2085 (1914); *ibid.*, **54**, 2353 (1921); *ibid.*, **55**, 3639 (1922).

5. Autoxidations.

Oxidation catalysts are useful in that they lower oxidation temperatures and provide for selectivity. In many cases, products are obtained which could not be otherwise.

Wieland[3, 4] is of the opinion that almost any oxidation can be interpreted as a removal of hydrogen from the substrate, or as a hydrogenation of the oxidizer. Consequently, the function of the catalyst is to loosen up the hydrogen directly from the substrate which is oxidized, or to take the oxygen from the oxidizer and carry it over on the substrate.

Frankenburger[5] concludes that, in most oxidation processes, labilization of the hydrogen of the oxidizable substance and activation of the oxygen by the catalyst or the inductor is brought about.

I. Inorganic reactions

(a) Liquid-Phase Reactions

Around the middle of the 19th century, extensive studies, on oxidation phenomena in liquid media, were made by Schoenbein[6, 7] who oxidized substances such as indigo (white), guaiac tincture, HI, P, As, Sb, etc., using as catalysts for these oxidations the salts and organic complex compounds of iron, cobalt, nickel, platinum, palladium, osmium, cerium, copper, silver, gold, and also of lead and mercury; furthermore, the salts and oxygen-containing radicals of chromium, tungsten, molybdenum, vanadium, magnesium, titanium, tellurium, and selenium. Schoenbein concluded that most of the oxidation reactions could take place without the aid of catalysts, but then only at substantially higher temperatures. For partial homogeneous catalytic oxidation of organic compounds, the salts of iron, copper and cerium are suitable, and so are the vanadates, molybdates, and chromates.[1, 5]

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[5] Frankenburger, W.: *Katalytische Umsetzungen in homogenen und enzymatischen Systemen*, Leipzig, Akademische Verlagsgesellschaft, 1937.

[6] Schoenbein: *J. prakt. Chem.*, **24**, 325 (1842); *ibid.*, **75**, 79, 101 (1858); *ibid.*, **78**, 90 (1858); *ibid.*, **86**, 99 (1862); *ibid.*, **89**, 32, 325 (1863): *ibid.*. **98**, 80, 340 (1866); *ibid.*, **105**, 202, 207 (1868).

[7] Schoenbein and Leibig: *J. prakt. Chem.*, (2), **18**, 292 (1878).

Schoenbein,[6,7] Loew,[9] and Traube and Biltz[10,11] studied the catalytic action of metallic copper in ammonia and the conversion of the ammonia to ammonium nitrite when air was passed through the solution. According to Traube, the conversion of ammonia to nitrite is due to the fact that molecular oxygen and the oxygen of the cupric oxide are carried simultaneously on to the ammonia. The cuprous oxide formed by this process is then oxidized to cupric oxide by the oxygen from the air. Consequently, the nitrite formation from ammonia proceeds as follows:

$$2CuO + NH_3 + O_2 \rightarrow HNO_2 + H_2O + Cu_2O$$
$$Cu_2O + \tfrac{1}{2}O_2 \rightarrow 2CuO$$

The absorption of oxygen by a solution of $Cu(OH)_2$, in ammonia, proceeds slowly, but oxygen is adsorbed very rapidly if metallic copper is present in the ammonia solution.

Iron and iron salts have catalytic properties similar to those of copper. In fact, traces of iron possess remarkable catalytic properties as oxygen carriers, which are of immense importance in living organisms and in nature.

A very illustrative study of the function of iron as a catalyst in nature has been made by Cronheim,[12] who studied the catalytic action of mineral waters from Saratoga Spa in decomposing hydrogen peroxide. This action was found to be due to ferrous ions in the water. The reaction mechanism is as follows:

1. $H_2O_2 \rightleftarrows H^+ + HO_2^-$
2. $Fe^{++} + H_2O_2 \rightarrow Fe^{+++} + OH + OH^-$

The OH-radical starts the following chain reaction:

3. $OH + H_2O_2 \rightarrow HO_2^- + H_2O$
4. $HO_2 \rightleftarrows H^+ + O_2^-$

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[9] Loew: *J. prakt. Chem.*, **20**, 568 (1882).
[10] Traube and Biltz: *Ber.*, **37**, 3130 (1904).
[11] Traube and Biltz: *Ibid.*, **39**, 166 (1906).
[12] Cronheim: *J. Phys. Chem.*, **45**, 328 (1941).

5. $O_2^- + H_2O_2 \rightarrow OH + OH^- + O_2$

$OH + H_2O_2 \rightarrow HO_2 + H_2O$, etc.

The chain can be broken by the reaction:

6. $OH + OH \rightarrow H_2O_2$

and perhaps by:

6a. $OH + HO_2 \rightarrow H_2O + O_2$

and:

6b. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

The ferric ion can be reduced as follows:

7. $Fe^{+++} + HO_2^- \rightarrow Fe^{++} + HO_2$

the HO_2-radical being able to start a new chain reaction. The slowest step in this mechanism is the oxidation of the ferrous iron to ferric ion.

The reaction mechanisms of iron and its compounds in enzyme reactions has been discussed by Wieland,[3] who made the important observation that the known catalytic effect of iron compounds is inhibited by hydrogen cyanide, carbon monoxide, and isonitriles in the same way as oxidation in living cells.

Cerium compounds[13, 14] are also very effective oxidation catalysts, glucose in alkaline solution being oxidized by the oxygen in the air in the presence of cerium oxide.

The oxidation of sugars to their corresponding acids, by dilute nitric acid (32% or stronger), is catalyzed by addition of a small amount, maximum five volume per cent, of fuming acid, which acts owing to the formation of nitrous acid.[15]

$$2NO_2 + HOH \rightarrow HNO_2 + HNO_3$$

The oxidizing action of nitric or nitrous acid is also catalyzed by vanadium and molybdenum compounds, and nitrates of iron

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[13] Job: *Compt. rend.*, **134**, 1052 (1902).

[14] Spoehr: *Compt. rend.*, **2**, 937 (1924).

[15] Kiliani: *Ber.*, **54**, 456 (1921).

or the rarer earths. By such reactions, cane sugar and wood are oxidized to oxalic acid.[15, 16]

The oxidative power of sulfuric acid is enhanced by the presence of mercury, copper, molybdenum, and platinum compounds. A mixture of copper and mercury compounds is much more active than the sum of the activities of the single components, when these catalysts are used in oxidation of aniline and naphthalene in hot concentrated sulfuric acid.[17]

A very good example of autoxidation was found by Bäckström [18, 19] in his study of the autoxidation of sodium sulfite in solutions, which takes place as a chain reaction and which is considerably accelerated by the action of ultraviolet light. Bäckström showed that each molecule which was thus activated can activate a large number of other molecules:

$$HSO_3^- \rightarrow HSO_3 + \epsilon$$

The HSO_3 radical, in the presence of dissolved oxygen, causes the following chain reaction:

$$\underset{\substack{\text{monothionic}\\\text{acid}}}{HSO_3} + O_2 + H_2O + SO_3^{--} \rightarrow 2SO_4^{--} + OH + 2H^+ \; *$$

$$OH + SO_3^{--} + H^+ \rightarrow \underset{\substack{\text{monothionic}\\\text{acid}}}{HSO_3} + OH^-, \text{ etc.}$$

This reaction is accelerated by heavy metal ions, especially copper:

$$Cu^{++} + HSO_3^- \rightarrow Cu^+ + HSO_3$$

Chain reactions, in oxidation, are provoked not only by light radiation, but also by heat and catalysts.[20, 21]

Haber and Weiz [22] interpreted the catalytic decomposition of

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[16] Neumann, Moeser and Lindenbaum: *J. prakt. Chem.*, (2), **75**, 148 (1907).

[17] Bredig and Brown: *Ber.*, **46**, 502 (1903).

[18] Bäckström: *J. Am. Chem. Soc.*, **49**, 1460 (1927).

[19] *Z. phys. Chem.*, **B 25**, 122 (1934).

[20] Baudisch: *Ber.*, **62**, 2699 (1929).

[21] Brunner et al.: *Z. physik. Chem.*, **A 139**, 453 (1928); *ibid.*, **154**, 161 (1929).

[22] Haber and Weiz: *Proc. Roy. Soc. (London)*, **A 147**, 332 (1934).

* This reaction proceeds with intermediate formation of a moloxide, HSO_5.

hydrogen peroxide, by iron salts, as a chain reaction proceeding as follows:

1. $Fe^{++} + H_2O_2 \rightarrow Fe^{+++} + OH^- + OH$
2. $OH + H_2O_2 \rightarrow H_2O + HO_2$
3. $HO_2 + H_2O_2 \rightarrow O_2 + H_2O + OH$, etc.

The chain is broken according to:

$$OH + Fe^{++} \rightarrow OH^- + Fe^{+++}$$

The length of the chains depends upon the relative concentrations of hydrogen peroxide, ferro and ferri salts, and the acidity of the solution.

(b) Inorganic Vapor-Phase Reactions

It is reported that oxidation of ammonia was the first catalytic process discovered, viz. by Milner,[23] in 1788, who used MnO_2 and calcined $FeSO_4$ as catalysts. Since then ammonia oxidation for production of nitric acid has become a huge industry. Ostwald[24] suggested platinum and Fe_2SO_4 as catalysts for the oxidation of ammonia. Franck and Caro[25] suggested oxides of the rare earths added to ThO_2. In 1914, Bosch, Mittasch, and Beck[26] took out a patent for using iron, cobalt, nickel, and the oxides of these metals to which bismuth trioxide was added, and a combination of iron and tungsten oxide. Later, in 1920, the I. G. Farbenindustrie[27] took out a patent for the use of platinum or a metal of the platinum group, with a layer of rhodium as a catalyst for oxidation of ammonia. Then, platinum-rhodium alloys were developed, and they are now used us gauzes containing 90 to 95 per cent of platinum, the remaining content being rhodium. These catalysts have been extensively investigated, and in studying the details of this important work, reference should be made to the original treatises.[28, 29, 30, 31]

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[23] Milner: *Trans. Roy. Soc. (London)*, **A 79**, 300 (1789). Passagez: *Ind. chim., belge*, **24**, 313 (1937); Berkman, Morrell and Egloff, *Catalysis—Inorganic and Organic*, New York, Reinhold Publishing Corp., 1940.

[24] Ostwald: U. S. Patent 858,904 (1902).

[25] Franck and Caro: German Patent 224,329 (1907).

[26] Bosch, Mittasch and Beck: German Patent 283,824 (1914).

[27] I. G. Farbenindustrie A.-G.: British Patent 331,728 (1920).

Catalytic reactions, for oxidation of sulfur dioxide and sulfurous acid, have received no less attention, as the huge sulfuric acid industry is dependent upon efficient catalysts in order to meet the keen competition which exists in this industry. The oxidation of sulfur dioxide, using nitrous oxides as catalyst, was investigated by Clement and Desormes,[32] at the beginning of the 19th century. Later, Phillips[33] suggested the use of platinum catalysts for this oxidation, but they were not adaptable to commercial-scale application, since at that time, no one knew how to avoid the poisoning of the catalysts by impurities in the reactants.

The contact process for oxidation of SO_2, using platinum as a catalyst, was not perfected until the beginning of this century, when Knietch[34] concluded his studies on the equilibrium: $2SO_2 + O_2 \rightleftharpoons 2SO_3$. It was then found that the best operating temperature was around 450°C, and an oxygen content in the reaction mixture of about three times the theoretical. Under these conditions about 98 per cent conversion was obtained. Knietch recognized the action of catalyst poisons and found out how to deal with them. The oxidation rate of SO_2 has been well studied and reference is made to a recent paper by Uyehara and Watson.[35] The contact process is especially useful for making oleum which is used in sulfonation and nitration processes.

A great variety of catalysts has been proposed for oxidizing SO_2 to SO_3, platinum metals,[33, 34, 35] vanadium oxide, and vanadates being favored.[36] Other catalysts, which have been sug-

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[28] Curtis, H. A.: *Fixed Nitrogen.* New York, Reinhold Publishing Corp., 1932.

[29] Handforth and Tilley: *Ind. Eng. Chem.*, **26**, 1287 (1934).

[30] Parsons: *Ind. Eng. Chem.*, **11**, 541 (1919); *ibid.*, **19**, 789 (1927).

[31] Taylor, Chilton and Handforth: *Ind. Eng. Chem.*, **23**, 860 (1931).

[32] Clement and Desormes: *Ann. chim.*, **59**, 329 (1809).

[33] Phillips: British Patent 6,096 (1831).

[34] Knietch: *Ber.*, **34**, 4069 (1901).

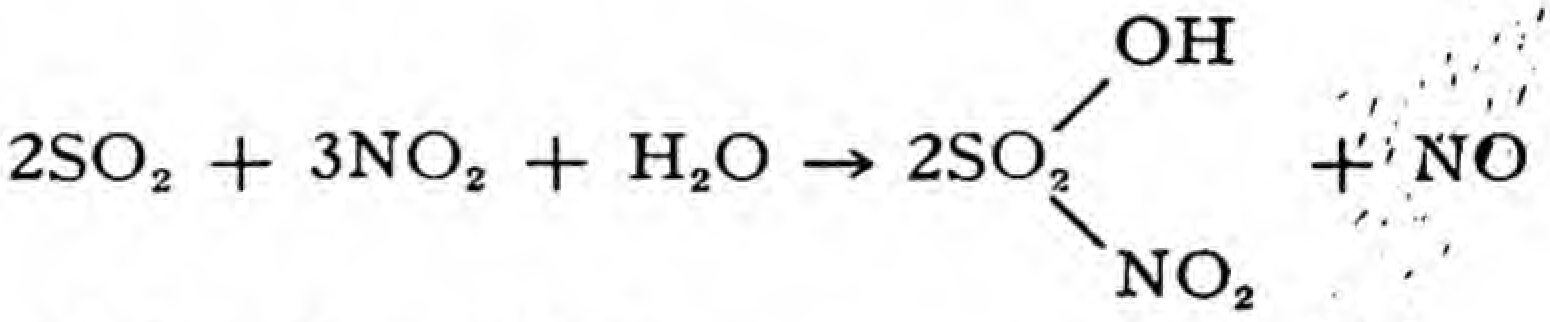
[35] Uyehara and Watson: *Ind. Eng. Chem.*, **35**, 541 (1943).

[36] Jaeger: *Ind. Eng. Chem.*, **21**, 627 (1929).

gested for oxidizing SO_2 to SO_3, are nickel boron silicate,[37] Na_2SiF_6,[38] rhenium alloy or oxide,[39] oxides on zeolites,[40] etc.

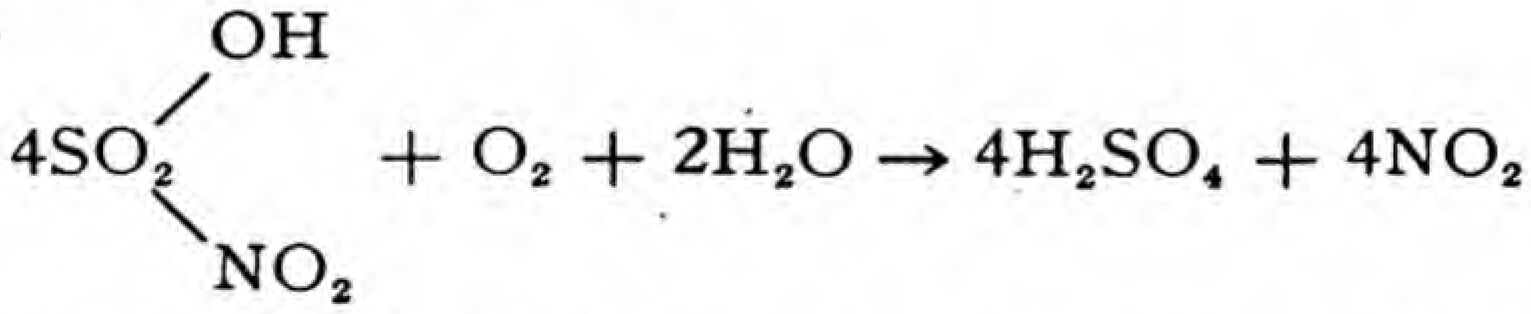
Several theories have been proposed for the acceleration of the oxidation of SO_2 by nitrogen oxides as it takes place in the lead chamber process, and although considerable literature exists on the subject, it appears that a final interpretation is still lacking.

Davy[41] (1812) is credited with the following reaction mechanism for converting SO_2 to SO_3 under the influence of nitrous oxides:

1. 

$$2SO_2 + 3NO_2 + H_2O \rightarrow 2SO_2\begin{matrix} OH \\ NO_2 \end{matrix} + NO$$

2. $2NO + O_2 \rightarrow 2NO_2$

3. 

$$4SO_2\begin{matrix} OH \\ NO_2 \end{matrix} + O_2 + 2H_2O \rightarrow 4H_2SO_4 + 4NO_2$$

Lunge and Berl[42] consider that nitrosyl sulfuric acid, $ONO \cdot SO_3H$, is an intermediate compound in this oxidation, although at times nitrosulfonic acid, $O_2N \cdot SO_3H$, may be formed.

Gas phase:
1. $2NO + O_2 \rightarrow 2NO_2$

Gas-liquid interphase:
2. $SO_2 + H_2O \rightarrow H_2SO_3$
3. $H_2SO_3 + NO_2 \rightarrow HO.NO \cdot SO_3H = \underset{\text{violet acid}}{SO_5NH_2}$
4. Oxidized with air or with nitrogen oxides (N_2O_3 resp. NO_2), depending on concentration:

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[37] German Patent 298,981 (1920).

[38] Niewenburg and Nooijer: *Rec. trav. chim.*, **47**, 627 (1928).

[39] French Patent 682,244.

[40] Jaeger: U. S. Patent 1,657,753 (1928).

[41] Davy: See Hilditch, T. P., and Hall, C. C.: *Catalytic Processes in Applied Chemistry*, London, Chapman & Hall, Ltd., 1937.

[42] Lunge and Berl: *Ber.*, **18**, 1884 (1885); *ibid.*, **21**, 67, 3225 (1888). *Z. angew. Chem.*, **19**, 807, 857, 881 (1906); *ibid.*, **20**, 1713 (1907).

$SO_5NH_2 \rightarrow \underset{\text{nitrosyl sulfuric acid}}{O\cdot NO\cdot SO_3H}$

Formation of sulfuric acid:

5. $2SO_5NH + SO_2 + 2H_2O \rightarrow 2SO_5NH_2 + H_2SO_4$

Liquid phase:

6. $SO_5NH_2 \rightarrow H_2SO_4 + NO$
7. $2SO_5NH + H_2O \rightarrow 2H_2SO_4 + NO + NO_2$
8. $SO_5NH + HNO_3 \rightarrow H_2SO_4 + N_2O_4$

Raschig[43] contends that nitrosyl sulfuric acid is not necessarily a substantial intermediary product, but rather an undesirable by-product.

1. $2NO + \frac{1}{2}O_2 \rightarrow N_2O_3$ and $2NO + \frac{1}{2}O_2 + H_2O \rightarrow 2HNO_2$
2. $HNO_2 + SO_2 \rightarrow NO\cdot SO_2\cdot OH$ *
3. $NO\cdot SO_2\cdot OH + HNO_2 \rightarrow NO + HO\cdot NO\cdot SO_2\cdot OH$
4. $HO\cdot NO\cdot SO_2\cdot OH \rightarrow H_2SO_4 + NO$

Phosphorus is oxidized—not necessarily catalytically, in the presence of water according to:

$$P_4 + 10H_2O \rightarrow 2P_2O_5 + 10H_2$$

This reaction is catalyzed by Fe_2O_3, bauxite, copper, or charcoal.[44] Coal gas, especially ethylene, retards this oxidation very much. The retarding action of negative catalysts does not change the phosphorus permanently.[45]

Hydrochloric acid[46, 47, 48] is oxidized to free chlorine and water:

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$$

This process is catalyzed by several metallic chlorides, especially $CuCl_2$ at 430 to 450°C. Deacon[46] and Hurter[48] interpreted the catalytic reaction as depending on intermediate formation of oxychlorides:

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[43] Raschig: *Liebigs Ann. Chem.*, **241**, 242 (1887); *ibid.*, **248**, 1236 (1888); *Ber.*, **21**, 3223 (1888); *Z. angew. Chem.*, **17**, 1398 (1904); *ibid.*, **18**, 1281 (1905).

[44] Liljenroth: U. S. Patent 1,594,372 (1926).

[45] Centnerszwer: *Z. physik. Chem.*, **85**, 99 (1913).

[46] Deacon: *J. Chem. Soc.*, **25**, 725 (1872).

[47] Hansenclever: *Ber.*, **9**, 1070 (1876).

[48] Hurter: *J. Soc. Chem. Ind.*, **2**, 103 (1883).

* May also form the hydrate, $HO\cdot NO\cdot HSO_2\cdot OH$.

1. $Cu_2Cl_2 + \frac{1}{2}O_2 \rightarrow CuO \cdot Cl_2$
2. $CuO \cdot Cl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$
3. $2CuCl_2 \rightarrow Cu_2Cl_2 + Cl_2$

Carbon monoxide, CO, is oxidized to carbon dioxide, CO_2, in the presence of finely divided nickel and cobalt at 350–450°C. Hopcalite,[49, 50, 51] a mixed manganese oxide catalyst of varying composition, oxidizes CO to CO_2 at ordinary temperature.

The oxidation mechanism of the Hopcalite catalysts has been studied by Pitzer and Frazer.[52] Frazer[53] also reports complete oxidation of carbon monoxide for unlimited time, at temperatures as low as –20°C in dry gas mixtures of carbon monoxide and oxygen, the catalyst used consisting of the oxides of nickel and cobalt. The oxidation of carbon monoxide is very important in the purification of exhaust gases, air-conditioning, etc.

II. Organic Oxidation Reactions

There have been so many investigations on the oxidation of organic compounds that it is hopeless to try to enumerate all of them, and only a few typical examples will be mentioned.

(a) Liquid-Phase Reactions

Rideal et al.[54] studied the reaction mechanism of non-catalyzed and heavy-metal-catalyzed oxidation of alkylbenzenes and long-chain, saturated aliphatic hydrocarbons (C_{15} to C_{25}) in the liquid phase at 100 to 120°C, with the conclusion that hydroperoxides are the primary oxidation products.

For alkylbenzenes, the peroxide formed corresponds to 60 to

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[49] Frazer and Scalione: U. S. Patent 1,345,323 (1920).

[50] Lamb: U. S. Patent 1,422,211 (1922).

[51] Lamb, Bray, and Frazer: *Ind. Eng. Chem.*, **12**, 217 (1920).

[52] Pitzer and Frazer: *J. Phys. Chem.*, **45**, 761 (1941).

[53] Frazer: U. S. Patent, 1,937,689 (1933).

[54] George, Rideal, and Robertson: *Nature*, **149**, 601 (1942).

80 per cent of the oxygen absorbed. The peroxides of long-chain paraffins are not so stable and are only found in a concentration of 5 per cent.

In the catalytic oxidation of long-chain praffins by cobalt stearate, and of alkylbenzene by copper stearate, the rate of oxidation is independent of the catalyst concentration above a certain value.

The catalyzed oxidation reaction is interpreted as following a chain mechanism in which the metallic catalyst both starts and stops the chain. The function of the metallic catalyst in hydrocarbon oxidation is considered to be threefold:

1. Start reaction chains leading to the production of peroxides.
2. Stop these chains.
3. Decompose the peroxide.

The rate of oxidation, ϕ, is expressed by:

$$\phi = \frac{a + by}{c + dy}$$

where y is the catalyst concentration, a the number of chains started per unit time in the non-catalyzed reaction and b the number of chains started per catalyst molecule; $1/c$ is the non-catalyzed chain length and $1/(c + dy)$ is the catalyzed chain length. For the catalyzed oxidation the following expression was derived:

$$\frac{dx}{dt} P = \alpha y$$

where dx/dt is the rate of oxidation, P the equilibrium peroxide concentration, y the catalyst concentration and α is a constant which is a measure of peroxide reactivity.

While discussing the oxidation of hydrocarbons, attention should be called to the work of Larson, Thorpe and Armfield[55] on oxidation characteristics of pure hydrocarbons. These authors found that all saturated hydrocarbons, paraffinic and cycloparaffinic, behave similarly on oxidation and that they are quite reactive. Aromatics, containing a benzene ring attached to a saturated side-chain or hydroaromatic ring, are still more reactive due to the activating influence of the aromatic ring. Polynuclear aromatics, however, are very stable, this being thought to be due to the formation of effective inhibitors upon oxidation. It was also concluded from this work that the stability of lubricating oils is due to a content of natural inhibitors and not to the stability of the basic hydrocarbons.

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[55] Larson, Thorpe and Armfield: *Ind. Eng. Chem.*, 34, 183 (1942).

In the oxidation of liquid and solid paraffins by air or oxygen to fatty acids,[56, 57, 58, 59, 60, 61] metallic salts, which are soluble in paraffins and oils, are used as catalysts, viz., stearates, palmitates, resinates, etc., of iron, copper, manganese, cerium, vanadium, and lead. This reaction is also accelerated by adding some previously oxidized paraffin.[60]

Oleates, linoleates, and resinates of cobalt, manganese, vanadium, uranium, and lead are used as oxidation catalysts in drying oils.

In linseed oil and any other vegetable oil consisting of triglycerides, the glyceride part of the molecules is adsorbed by and oriented toward the metal catalyst, whereas the paraffin part, with its active double bonds, is oriented toward the bulk of the oil. If a contact, rich in carbon, is introduced into the linseed oil, the CH-poles will orient themselves toward this contact, and retardation of the oxidation will result. Consequently, lamp black, graphite, asphalt, and a great number of organic dyes retard the oxidation of linseed oil.[62]

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[56] Franck: *Chem. Ztg.*, **44**, 309, 742 (1920).

[57] Grüen: *Ber.*, **53**, 987 (1920).

[58] James: *Chem. Met. Eng.*, **26**, 209 (1922).

[59] Kelber: *Ber.*, **53**, 66 (1920).

[60] Pardubitzer Fabrik der Aktiengesellschaft für Mineralöl-Industrie, vorm. David Fanto and Co.: British Patents 131,301 (1919), 131,302 (1917) and 131,303 (1918).

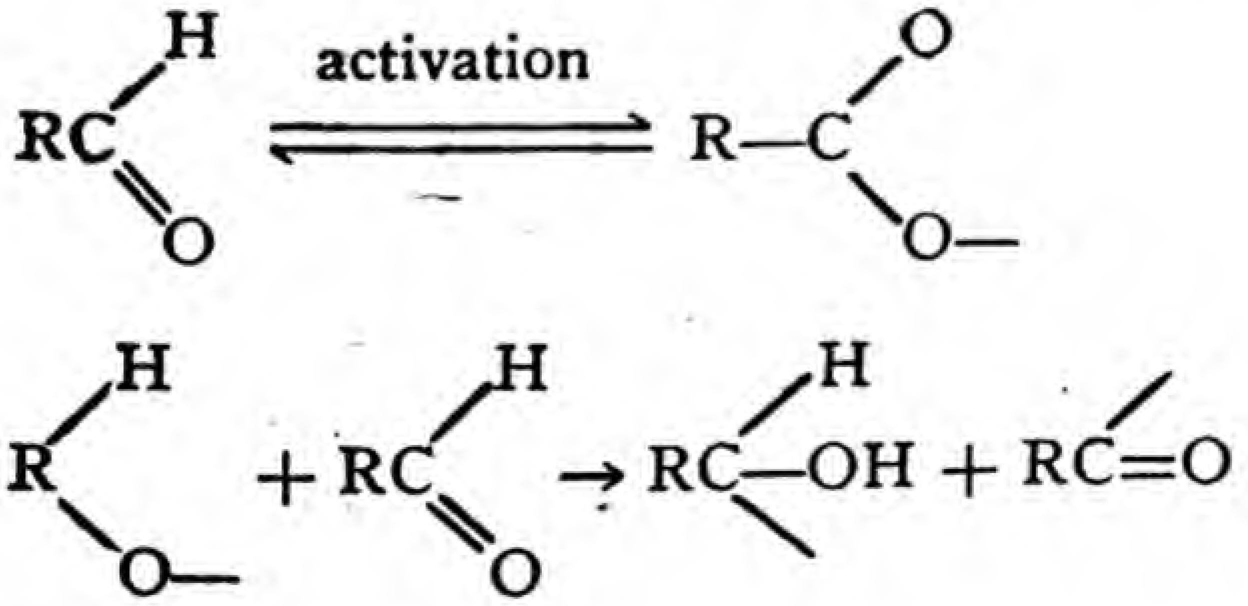
[61] Reid: U. S. Patent 1,663,523 (1928); Reid and Burke: U. S. Patent 1,663,524 (1928).

[62] Slansky: *Chem. Umschau Fette, Öle, Wachse, Harze*, **31**, 281 (1924); Berkman, Morrell and Egloff: *Catalysis—Inorganic and Organic*, New York, Reinhold Publishing Corp., 1940, p. 543.

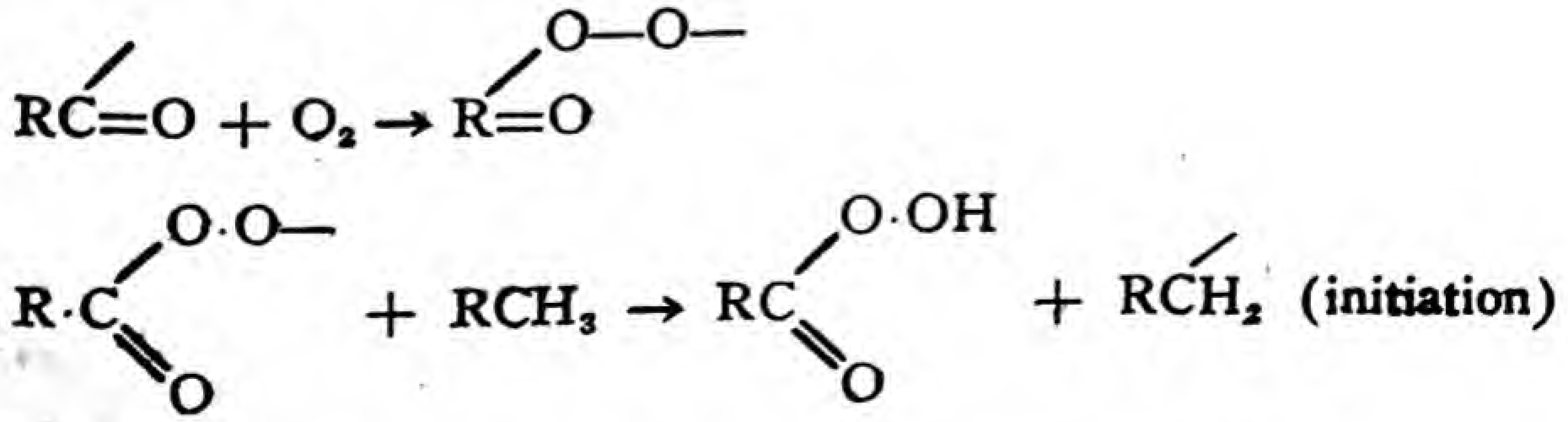
For oxidation of paraffins, Kelber[59] uses as catalysts the lower manganese oxides, manganese silicate, osmium, and platinum, the principle being to select catalysts that do not dissolve in the resulting acids. Elementary oxygen oxidizes paraffin, without the aid of catalysts. If the oxidation is not controlled, all kinds of fatty acids may be formed, and by using pure oxygen, intermediary moloxides, containing oxygen in the form of peroxide combinations, may give rise to explosions. Conversion of paraffins to fatty acids, up to 100 per cent, have been reported.

The mechanism of oxidation of paraffins has been carefully studied by Ubbelohde,[63, 64] who concludes that a hydrocarbon molecule must be dehydrogenated before it can be oxidized. Consequently, dehydrogenating substances must be added or formed during the process if they are not present. The dehydrogenation takes place in heterogeneous reactions during the period of induction. An aldehyde is formed first and next an aldehyde peroxide. Such a mechanism has first been suggested by Bäckström.[18, 19] The reaction mechanism is as follows:

1.



Followed by



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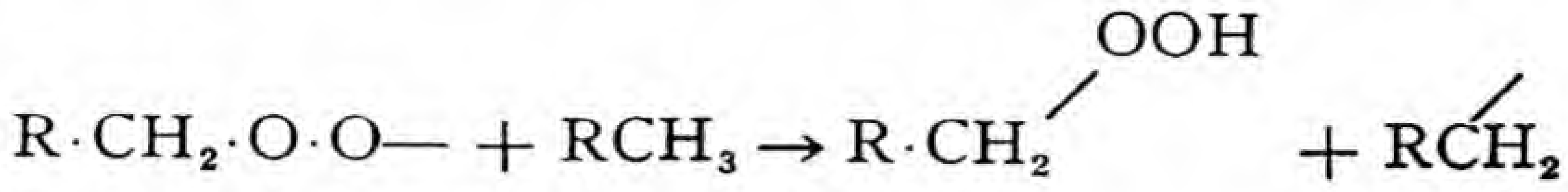
[63] Jost, Muffling, and Rohrmann: *Z. Elektrochem.*, **42**, 488 (1936).

[64] Ubbelohde: *Proc. Roy. Soc. (London)*, **A 152**, 354 (1935); *Z. Elektrochem.*, **42**, 468 (1936).

3. $R\cdot\overset{/}{C}H_2 + O_2 \rightarrow RCH_2\cdot O\cdot O\text{—}$ (propagation)

4. 

$$R\cdot CH_2\cdot O\cdot O\text{—} + RCH_3 \rightarrow R\cdot CH_2\overset{\quad OOH}{\diagup} \quad + R\overset{/}{C}H_2$$

5. Break of the reaction chain

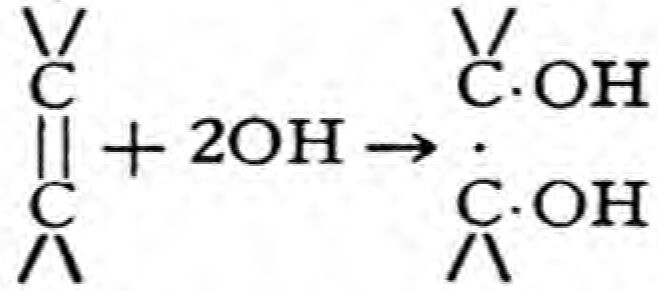
Haber and Willstätter[65] interpret the oxidation of aldehydes to acids as a chain reaction, in which, the single chains start by dehydrogenation of the aldehyde:

$$R\cdot CHO + Me^{+++} \rightarrow Me^{++} + H^+ + R\cdot CO$$
$$R\cdot CO + R\cdot CHO + O_2 + H_2O \rightarrow 2R\cdot COOH + \underset{|}{OH}$$
$$\underset{|}{OH} + RCHO \rightarrow R\cdot\underset{|}{CO} + H_2O, \text{ etc.}$$

It is also here assumed that as an intermediary step, a radical, $R\cdot\underset{\underset{\textstyle O\cdot O\text{—}}{\cdot}}{C}:O$ is formed.

Hydroxylation of unsaturated hydrocarbons, by hydrogen peroxide in anhydrous tert-butyl alcohol in the presence of catalysts, or by the action of ultraviolet light, has been carried out by Milas et al.,[66] who made a series of hydroxy compounds in this way. It was found that light, in the region of 3000 Å, causes the hydrogen peroxide to dissociate into hydroxyl radicals (*J. Am. Chem. Soc.*, **59**, 543, 1937):

$$HO\cdot OH + h\nu \rightarrow 2\underset{\cdot}{OH}$$



$$\begin{matrix} \diagdown\diagup \\ C \\ \| \\ C \\ \diagup\diagdown \end{matrix} + 2OH \rightarrow \begin{matrix} \diagdown\diagup \\ C\cdot OH \\ \cdot \\ C\cdot OH \\ \diagup\diagdown \end{matrix}$$

The same reaction takes place in the presence of osmium tetroxide, vanadium pentoxide, and chromium trioxide. The data are as follows:

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[65] Haber and Willstätter: *Naturwissenschaften*, **64**, 2844 (1931).

Unsaturated hydrocarbon	Main product	OsO_4	V_2O_5	CrO_3
Trimethylethylene	Trimethylethylene glycol	40	36.4, 37.3	16.8
Diethyl fumarate	Diethyl racemate	..	57	...
Anethole	Anisaldehyde	..	55	13.7
Isoeugenol	Vanillin	..	66	58.3
Isosafrole	Piperonal	..	67.5	14.0
Benzene	Phenol	..	30	12.2
Ethylene	Ethylene glycol	88, 23, 97	...	...
Propylene	Propylene glycol	68	...	...
Styrene	Phenyl glycol	50	...	...
Isobutylene	Isobutylene glycol	38	...	...
d-Limonene	p-Menthane tetrol-l, 1, 2, 8, 9	35	...	...

Other hydrocarbons were oxidized, the results being similar. The glycols produced were almost invariably of cis-configuration.

Oxidation in the Vapor Phase

Methane can be oxidized by a variety of catalytic processes:

1. $CH_4 + 2H_2O \xrightarrow{W + CeO_2} CO_2 + 4H_2$[67]

2. $CH_4 + O_2 \xrightarrow{\text{supported Cu}} CH_2O + H_2O$[68]

3. $2CH_4 + O_2 \xrightarrow[\text{Fe, Co, Ni, or oxides; } MnO_2,\ NiO,\ Co_2O_3]{\text{Pt, Pd, Ag, Cu}} 2CO + 4H_2$[69, 70, 71]

4. $CH_4 + CO_2 \xrightarrow[900\text{–}1000^\circ C]{\text{Co or Ni on } Al_2O_3} 2CO + 2H_2$[72, 73]

The slow oxidation of hydrocarbons, in general, has been extensively studied by Bone,[74] who showed that aldehydes and acids were formed as intermediate compounds in such oxidation. This evidence was obtained by a study of slow combustion. The inter-

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[66] Milas et al.: *J. Am. Chem. Soc.*, **58**, 1302 (1936); *ibid.*, **59**, 543, 2342, 2345 (1937).

[67] L'Azote, Inc.: U. S. Patent 1,713,325 (1927).

[68] Bone and Wheeler: *J. Chem. Soc.*, 1074 (1903).

[69] Bone and Andrew: *J. Chem. Soc.*, 78 (1906).

[70] German Patent 403,049 (1922).

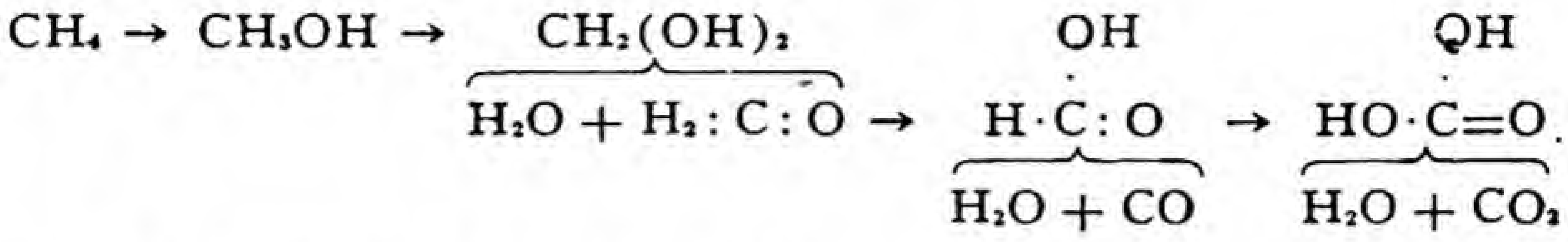
[71] Jant and Hawk: *J. Am. Chem. Soc.*, **49**, 1459 (1927).

[72] Fischer and Tropsch: *Brennstoff-Chem.*, **9**, 39 (1928).

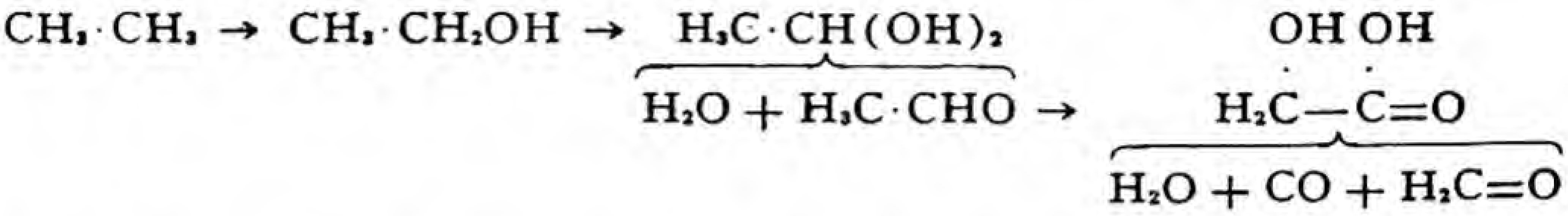
[73] Lang: *Z. phys. Chem.*, **2**, 161 (1888).

[74] Bone: *Trans. Roy. Soc. (London)*, **A 137**, 243 (1932).

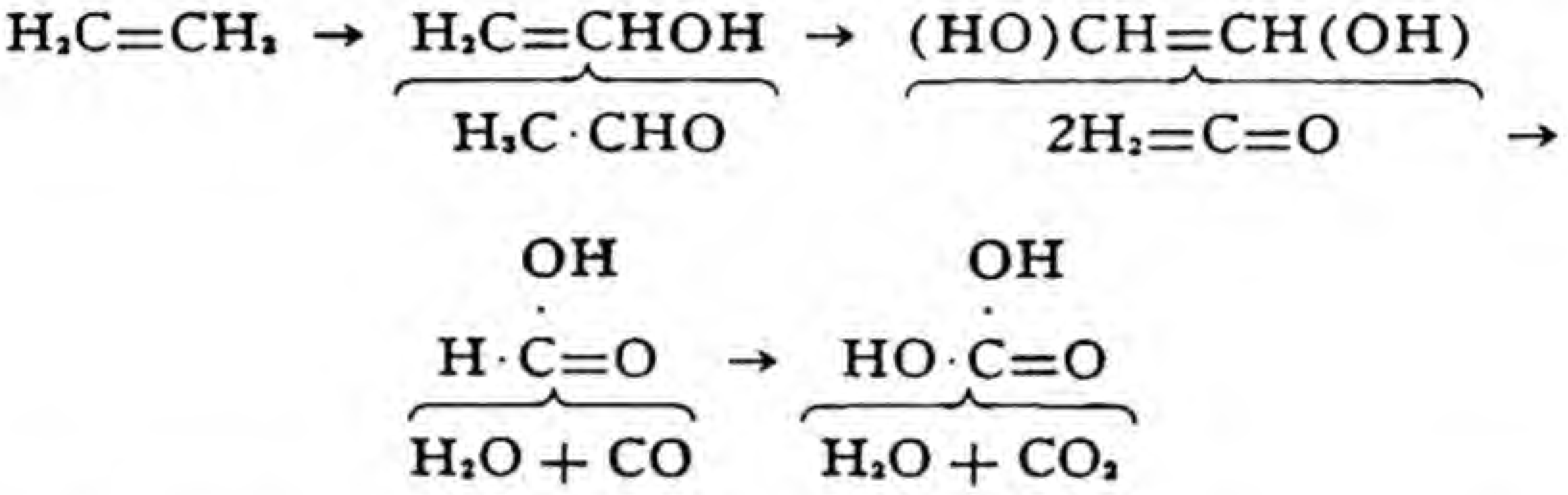
mediate compounds, formed in the oxidation of various hydrocarbons, were as follows:

1. 

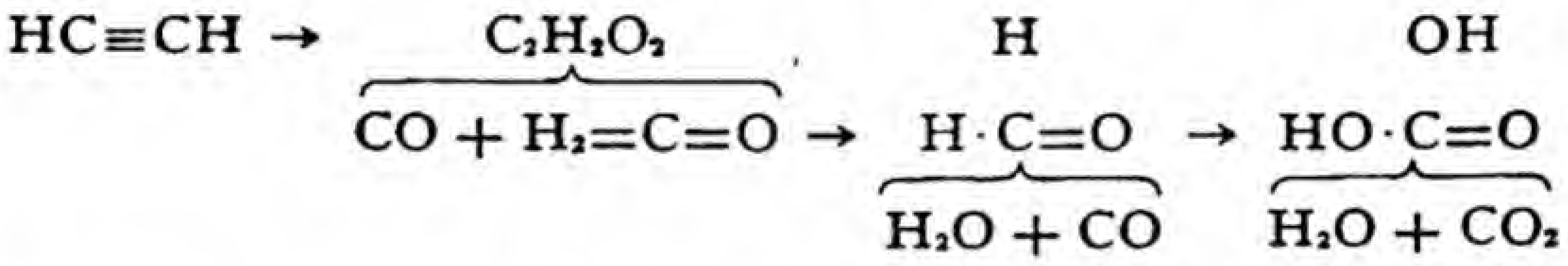
$$CH_4 \rightarrow CH_3OH \rightarrow \underbrace{CH_2(OH)_2}_{H_2O\,+\,H_2:C:O} \rightarrow \underbrace{H\cdot\overset{OH}{C}:O}_{H_2O\,+\,CO} \rightarrow \underbrace{HO\cdot\overset{OH}{C}{=}O}_{H_2O\,+\,CO_2}$$

2. 

$$CH_3\cdot CH_3 \rightarrow CH_3\cdot CH_2OH \rightarrow \underbrace{H_3C\cdot CH(OH)_2}_{H_2O\,+\,H_3C\cdot CHO} \rightarrow \underbrace{H_2\overset{OH}{C}{-}\overset{OH}{C}{=}O}_{H_2O\,+\,CO\,+\,H_2C{=}O}$$

3. 

$$H_2C{=}CH_2 \rightarrow \underbrace{H_2C{=}CHOH}_{H_3C\cdot CHO} \rightarrow \underbrace{(HO)CH{=}CH(OH)}_{2H_2{=}C{=}O} \rightarrow \underbrace{H\cdot\overset{OH}{C}{=}O}_{H_2O\,+\,CO} \rightarrow \underbrace{HO\cdot\overset{OH}{C}{=}O}_{H_2O\,+\,CO_2}$$

4. 

$$HC{\equiv}CH \rightarrow \underbrace{C_2H_2O_2}_{CO\,+\,H_2{=}C{=}O} \rightarrow \underbrace{H\cdot\overset{H}{C}{=}O}_{H_2O\,+\,CO} \rightarrow \underbrace{HO\cdot\overset{OH}{C}{=}O}_{H_2O\,+\,CO_2}$$

A very important study, on direct oxidation of natural gasoline hydrocarbons at high pressures, has been made by Wiezevich and Frolich.[75] Most experiments were carried out with a natural gas containing 2.1% ethane, 6.3% propane, 5% nitrogen, the balance being methane. The pressures used were around 135 to 170 atmospheres, and the temperature between 300 and 400C. Methyl alcohol was present in preponderance among the desirable products (3 to 8 times the amount of formaldehyde). Formic acid was also formed and so was water. The products were chiefly derived from the ethane in the gas as the temperature was too low for methane to react.

Increase in pressure tends to lower the temperature at which oxidation takes place and to retard the decomposition of intermediate products. It was also found that metallic catalysts (chromel, silver, etc.) gave better results than empty tubes.

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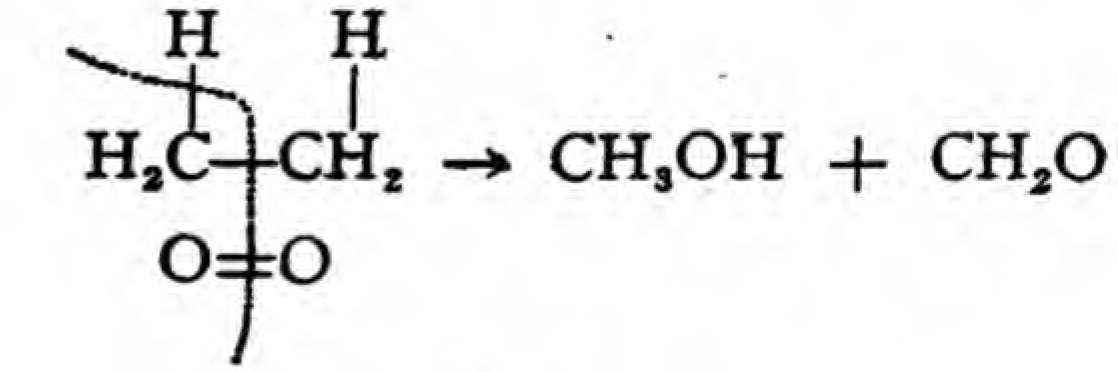
[75] Wiezevich and Frolich: *Ind. Eng. Chem.*, 26, 267 (1934).

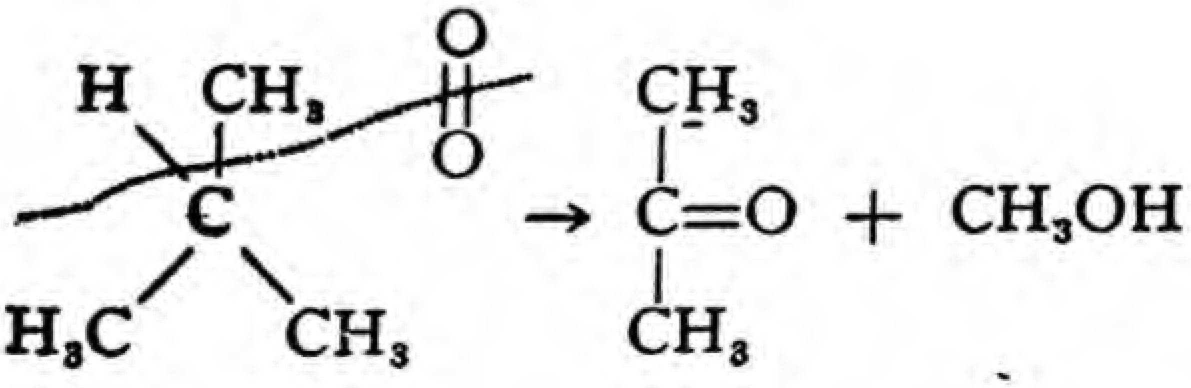
A typical run with a natural gas, containing 2.1% ethane, 0.3% propane, the balance being methane, at 135 atmospheres pressure and a temperature of about 390°C, and with 5.4% inlet oxygen, yielded a liquid product of a specific gravity of 0.953, analyzing about 30.3% methyl alcohol, 3.3% formaldehyde, and 0.5% formic acid. This means that 16.2% of the inlet oxygen was present in desirable products, and 3.7% of the ingoing carbon was converted to methyl alcohol, formaldehyde, and formic acid. One cubic meter of this natural gas yielded:

0.0615 liters of methyl alcohol
0.008 liters of formaldehyde (liquid)
0.0004 liters of formic acid.

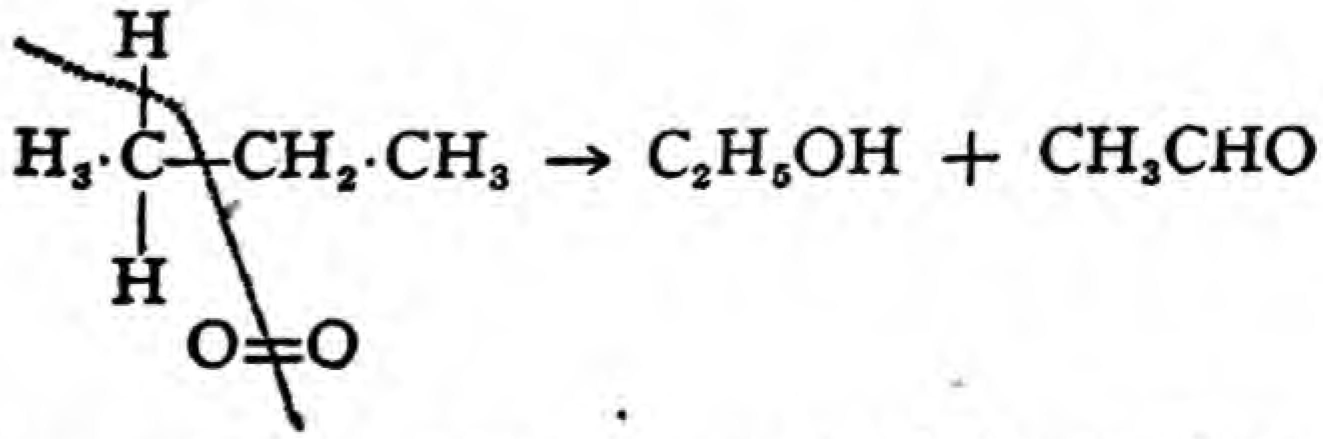
At relatively high temperature, some of the methane is converted into methanol. The higher hydrocarbons undergo carbon-to-carbon scission with the formation of lower derivatives in high yields:



$$H_2C{-}CH_2 + O{=}O \rightarrow CH_3OH + CH_2O$$



$$(CH_3)_3CH + O{=}O \rightarrow CH_3{-}CO{-}CH_3 + CH_3OH$$



$$H_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + O{=}O \rightarrow C_2H_5OH + CH_3CHO$$

A vast amount of work has been carried out along these lines. An interesting mechanism for the conversion of methyl alcohol to formaldehyde, using vanadian oxide as catalyst, is as follows:[75a]

1. $6CH_3OH + V_2O_5 \rightarrow 2(CH_3)_3VO_4 + 3H_2O$
2. $2(CH_3)_3VO_4 + 2H_2O \rightarrow V_2O_4 + 5CH_3OH + CH_2O$
3. $2(CH_3)_3VO_4 + H_2O \rightarrow V_2O_3 + 4CH_3OH + 2CH_2O$

At lower temperatures (270 to 325°C), reaction (1) is believed to predominate, whereas at higher temperatures (up to 400°C), reaction (3) predominates. Addition of oxygen, up to the theoretical limit, increases the yield because the reaction is controlled by the formation of intermediate oxides.

Patterson and Day[76] studied the catalytic conversion of primary alcohols to aldehydes and found that this reaction consisted in two distinct steps:

(1) Dehydrogenation of the alcohol to the aldehyde:

$$C_2H_5OH \rightarrow CH_3CHO + H_2$$

(2) Partial or complete oxidation of the hydrogen formed in the first step, this reaction furnishing the energy necessary to maintain the reaction:

$$2H_2 + O_2 \rightarrow 2H_2O$$

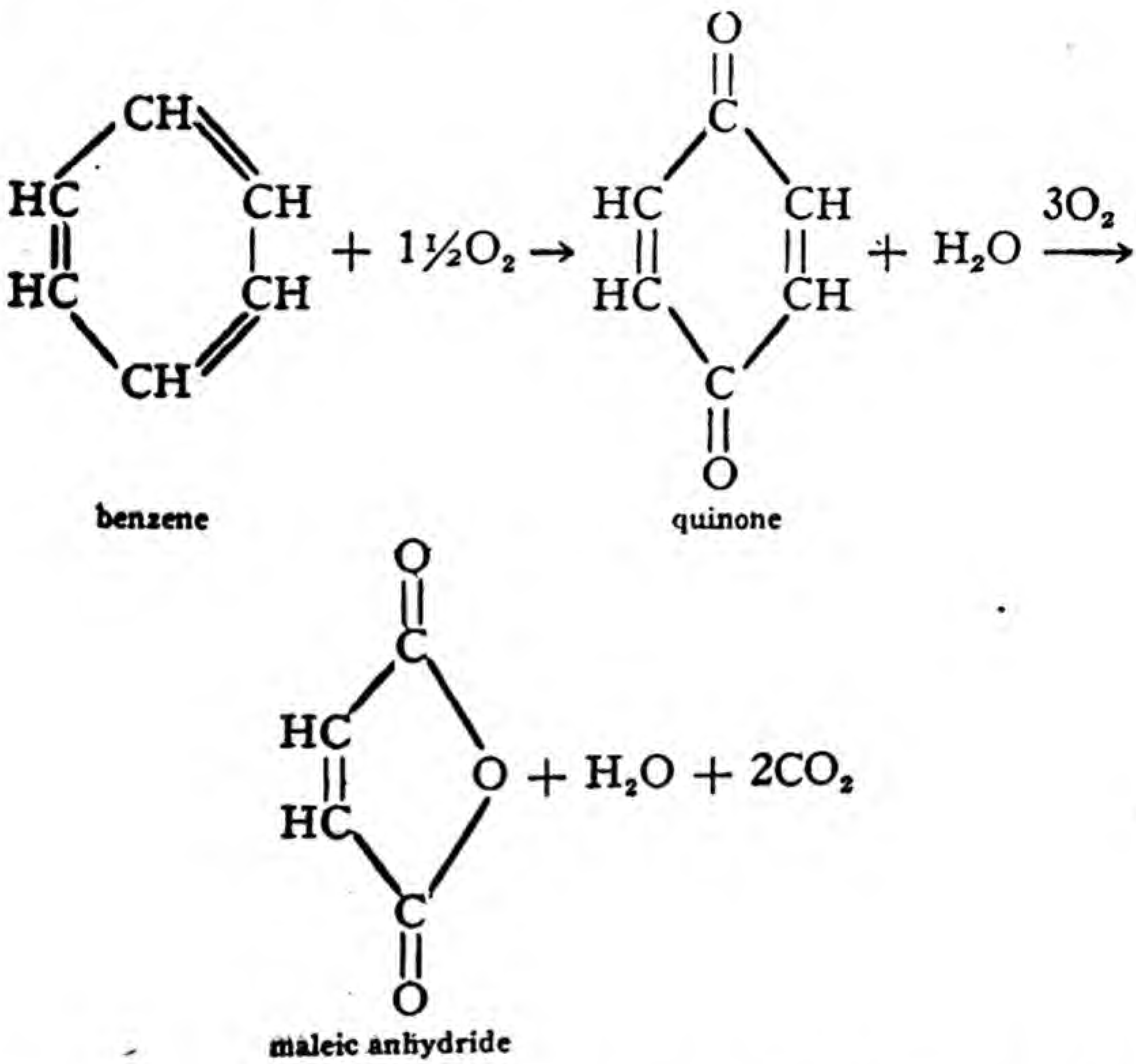
Experiments were carried out at 1 to 50 atmospheres of pressure of the alcohol over a silver catalyst, and at 1 atmosphere over a silver catalyst promoted with samarium oxide. The conversion decreased rapidly with increase in pressure. The promoted catalyst has the advantage of increasing the yields of acetaldehyde, and of permitting efficient operation at a somewhat lower temperature than the unpromoted catalyst. The optimum temperature is between 370 and 415°C.

Oxidation of aromatic compounds is of considerable industrial importance, and a few examples are mentioned here in order to complete this brief review.

[75a] Canneri and Cozzi: *Chimica Industria* (Italy), **21**, 653 (1939); *Chem. Abstracts*, **34**, 3237 (1940).

[76] Patterson and Day: *Ind. Eng. Chem.*, **26**, 1376 (1934).

Benzene is oxidized by air, in the vapor phase, in contact with V_2O_5, to maleic anhydride: [77]



Toluene is oxidized to benzaldehyde and benzoic acid over vanadium oxide as catalyst. Numerous other catalysts have also been suggested.[40, 48, 78, 79]

Naphthalene is oxidized in the vapor phase with air at 300 to 500°C over V_2O_5 or MoO_3: [77, 78, 80, 81]

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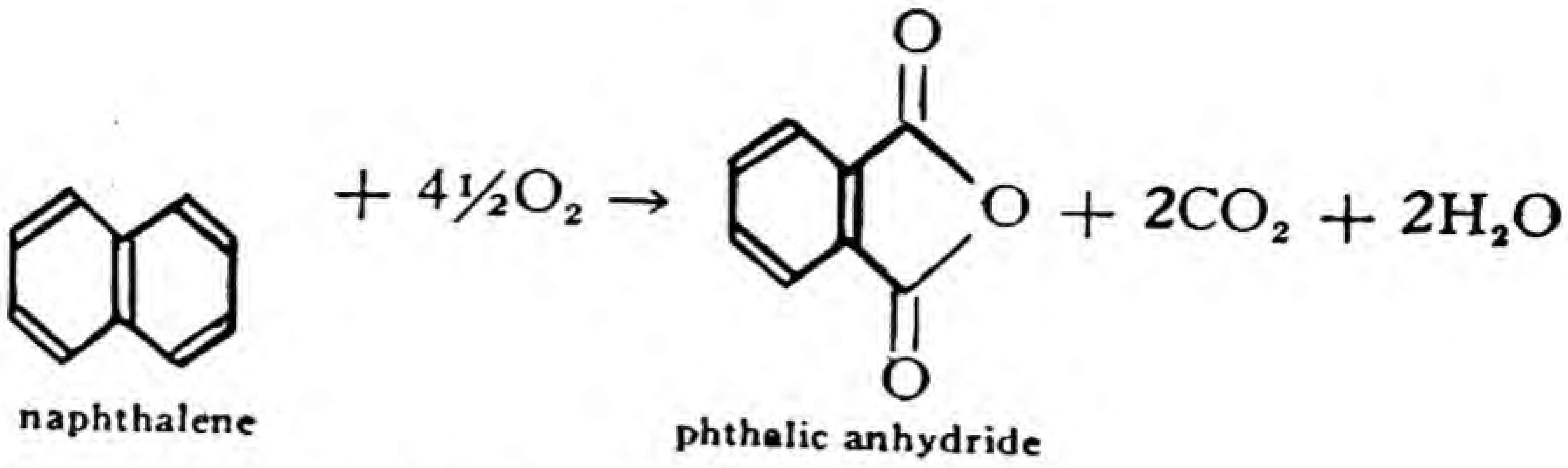
[77] Weiss and Downs: *Ind. Eng. Chem.*, **12**, 228 (1920); **26**, 17 (1934); *J. Soc. Chem. Ind.*, **45**, 188T (1926).

[78] Jaeger: *Ind. Eng. Chem.*, **20**, 1330 (1928).

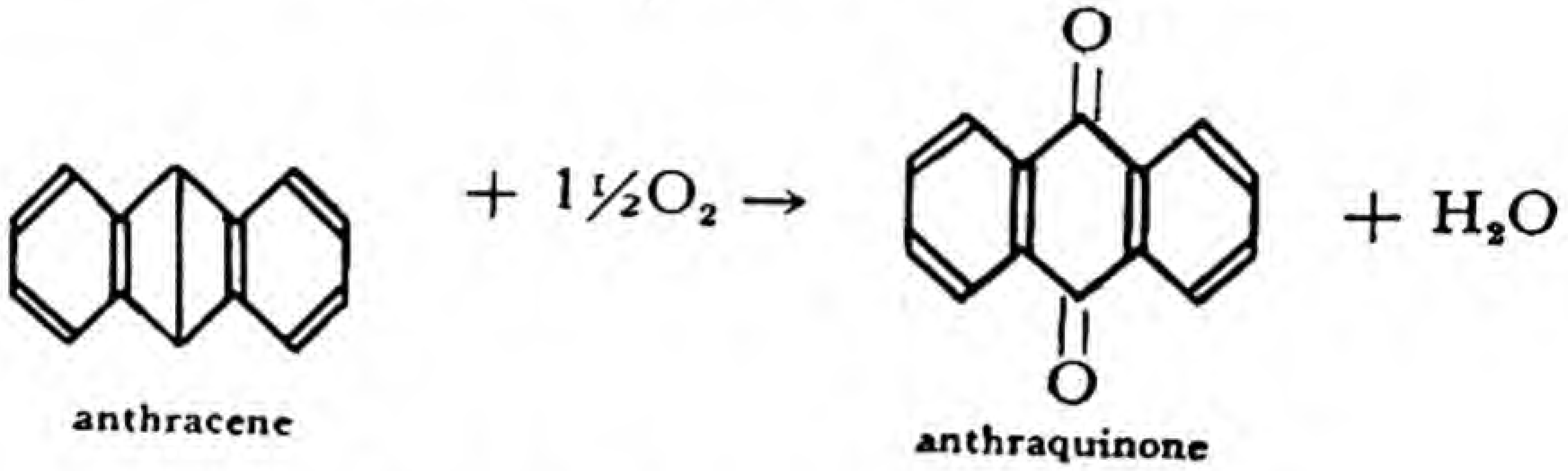
[79] Jaeger: U. S. Patents 1,694,122 (1928) and 1,935,054 (1933).

[80] Conover and Gibbs: U. S. Patent 1,417,367 (1922).

[81] The Selden Company and H. Drake Gibbs: British Patents 119,517 and 119,518 (1918). Craver: U. S. Patent 1,489,741 (1924).



Anthracene is oxidized over the same catalysts:



GENERAL REFERENCES

James, *Trans. Amer. Inst. Chem. Eng.*, **14**, 189 (1921); Bittler and James, *ibid.*, **20**, 95 (1927); Mittasch, Willforth and Balz, U. S. Patent 1,487,020 (1924); Emmett Reid and Burke, U. S. Patent 1,663,524 (1928); James, U. S. Patent 1,858,095 (1932); Walker, U. S. Patent 2,007,116 (1935); Gutehoffnungshütte Oberhausen A. G., British Patent 520,480 (1940); Genthe: *Z. angew. Chem.*, **19**, 2087 (1906); Kissling: *Z. angew. Chem.*, **4**, 395 (1891); Lippert: *Z. angew. Chem.*, **11**, 412 (1898); Marek: Private Communication, 1943; Marek, L. F. and D. Hahn: *The Catalytic Oxidation of Organic Compounds in the Vapor Phase*, New York, Reinhold Publishing Corp., 1932; Marek, L. F.: Oxidation Chapter VII of *Unit Processes in Organic Synthesis*, New York, McGraw-Hill Book Co., Inc., 1938; Parks and Katz: *Ind. Eng. Chem.*, **28**, 319 (1936); Weiss and Downs: U. S. Patent 1,355,098 (1920).

2. Dehydrogenation

According to Sabatier[1] the metals, which act as hydrogenation catalysts (nickel, copper, platinum metals), can also remove hydrogen contained in other compounds. This removal of hydrogen atoms from organic compounds is termed dehydrogenation, and as a catalytic process, it is gaining in importance as it renders possible to prepare unsaturated compounds from saturated ones, to make aldehydes and ketones from alcohols, and to change straight-chain compounds into cyclic ones.

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[1] Sabatier, P.: *La Catalyse en Chemie Organique*, Librairie Polytechnique, Paris, 1920; P. Sabatier and E. Emmett Reid: *Catalysis in Organic Chemistry*, New York, D. Van Nostrand Co., 1923.

Benzene is converted into cyclohexane by hydrogenation over reduced nickel between 70 and 200°C, but at 270 to 280°C, the cyclohexane is dehydrogenated in the presence of the same catalyst. In other words, the dehydrogenation process is reversible:[2,3,4,5,7]

$$C_6H_6 + 3H_2 \underset{\text{high temperature}}{\overset{\text{low temperature}}{\rightleftharpoons}} C_6H_{12}$$

Later, it has been found that suitable catalysts for dehydrogenation of gaseous paraffins are solid catalysts containing minor molar proportions of the oxides of the transition metals of the sixth group (e.g., chromium and molybdenum), fifth group (e.g., vanadium), and the fourth group (e.g., titanium and cerium), of the periodic system, supported on carriers of relatively low catalytic activity, such as aluminum and magnesium oxides.[5]

Paraffins are dehydrogenated at high temperatures, whereas olefins combine with hydrogen at low temperature:[5]

$$C_nH_{2n+2} \underset{\text{decrease in temperature}}{\overset{\text{increase in temperature}}{\rightleftharpoons}} C_nH_{2n} + H_2$$

The approximate equilibrium constants are calculated from:

$$K_p = \frac{[C_nH_{2n}][H_2]}{[C_nH_{2n+2}]}$$

Under suitable conditions for the dehydrogenation, 90 to 95 per cent, or more, of the theoretical conversion is obtained, simultaneously with an equal volume of practically pure (over 90 per cent) hydrogen.

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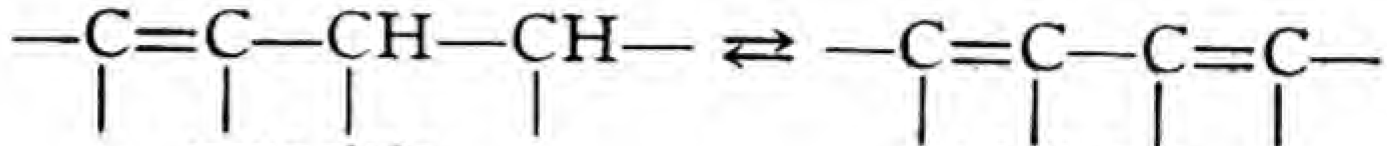
[2] Sabatier and Senderens: *Compt. rend.*, **132**, 210 (1901).
[3] Sabatier and Mailhe: *Ibid.*, **137**, 240 (1903).
[4] Sabatier and Daudier: *Ibid.*, **168**, 670 (1919).
[5] Grosse and Ipatieff: *Ind. Eng. Chem.*, **32**, 268 (1940).
[7] Pitzer: *Ibid.*, **5**, 473 (1937).

Another very important reaction is the dehydrogenation of mono-olefins to di-olefins:[8] 1,3-butadiene is formed from n-butenes, isoprene from branched chain pentenes, and piperylene from 2-pentene. The catalysts used are the same as used by Grosse and Ipatieff,[5] i.e., Cr-, Mo-, or V-oxide on alumina. The di-olefins formed are of the conjugated type, and have the same carbon framework as the parent olefin:



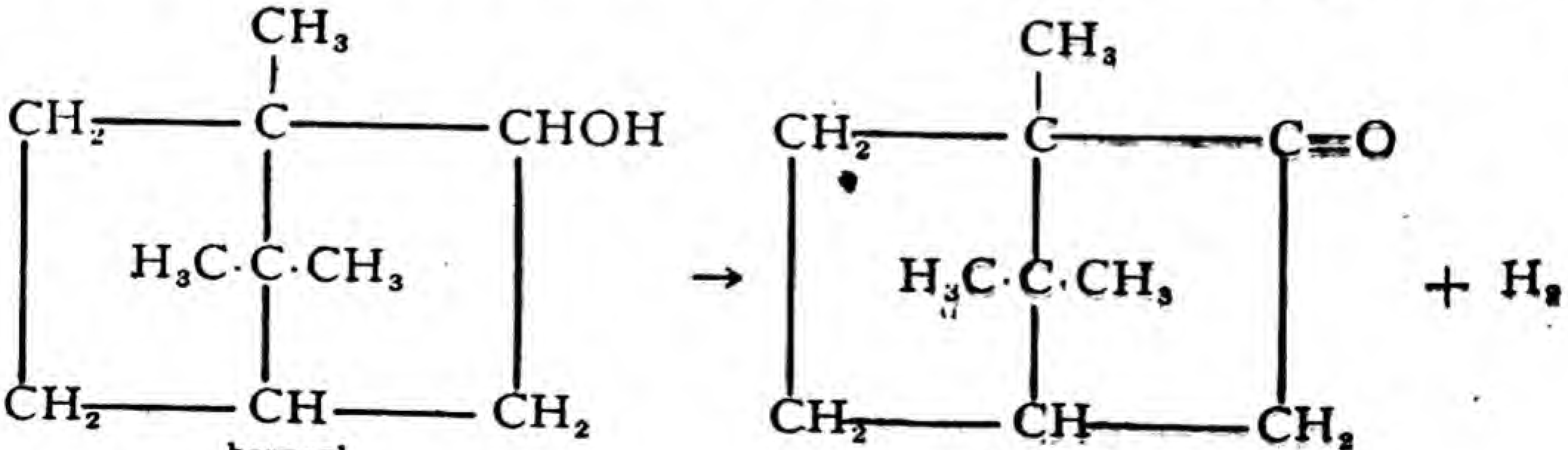
$$-\mathrm{C}=\mathrm{C}-\mathrm{CH}-\mathrm{CH}- \rightleftarrows -\mathrm{C}=\mathrm{C}-\mathrm{C}=\mathrm{C}-$$

mono-olefin 1,3-di-olefin

The equilibrium of this reaction is shifted to the right with rise in temperature. As the reaction to the right represents an increase in the number of mols, it is favored by decrease in pressure. Due to this, the reactions were carried out at 0.25 atmospheres pressure or lower, and in most cases, at temperatures of 600 to 650°C.

A very considerable amount of work on dehydrogenation has been undertaken by the Shell Development Company, and only lack of space prevents us from giving a detailed discussion of their work here.[9]

Borneol and isoborneol are dehydrogenated to camphor industrially, Zn, Ag, Cd, Cu, Ni, or Al_2O_3 being used as catalysts.[10, 11, 12]



borneol camphor

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[8] Grosse, Morrell, and Mavity: *Ind. Eng. Chem.*, **32**, 309 (1940).

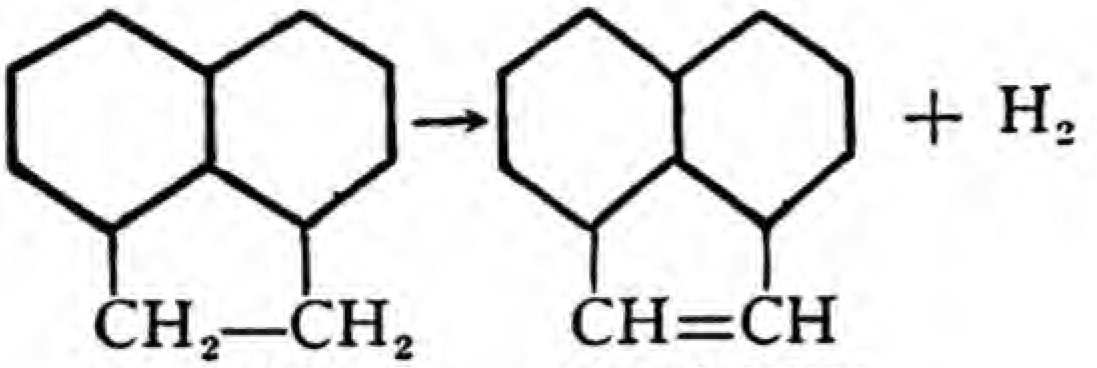
[9] Williams, E. C. and M. de Simo: *Catalytic Dehydrogenation of Oxy-organo Compounds*, Chapter VII, p. 92; *Dehydrogenation of Hydrocarbons*, Chapter IX, p. 98. Twelfth Report of the Committee on Catalysis, National Research Council, New York, John Wiley and Sons, 1940.

[10] Woog: *Compt. rend.*, **145**, 124 (1907).

[11] Ipatieff: *Ber.*, **45**, 3205 (1912).

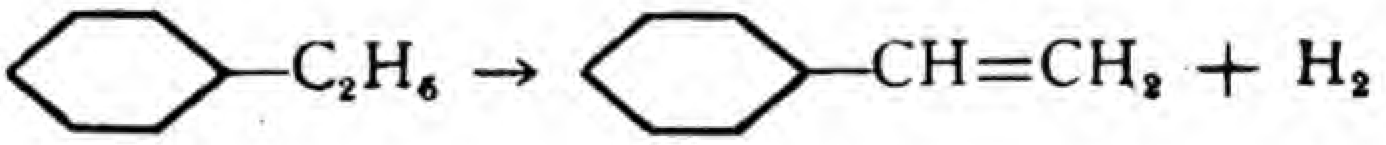
[12] Du Pont de Nemours, I. E. and Co., Inc.: British Patent 392,134 (1933).

Acenaphthene is dehydrogenated to acenaphthylene at 500 to 800°C, using as catalyst oxides of the alkaline earths and oxides of metals of the second to the fourth groups of the periodic system, e.g., mixtures of $ZnMoO_4$ and MgO, or ZnO and Al_2O_3.[13]



acenaphthene **acenaphthylene**

Ethyl benzene is dehydrogenated to styrene using oxides of Ce, Zn, W, U, Mo, or Si as catalysts.[14]



In the presence of Cr_2O_3, ethyl benzene is dehydrogenated to styrene between 425 and 525°C.[15] The lower paraffins are dehydrogenated to olefins over activated alumina catalyst.[16] Ethyl alcohol is dehydrogenated to acetaldehyde using such catalysts as reduced copper at about 300°C or oxides, e.g., SnO, Mn_3O_4, CdO, or MgO at 340 to 350°C.[17, 18, 19]

$$CH_3{\cdot}CH_2OH \rightarrow CH_3CHO + H_2$$

When copper catalysts are heated above 400°C, they sinter with permanent loss of their activity.[19]

Butyl alcohol is readily dehydrogenated to butyl aldehyde over a rhenium catalyst at 350 to 450°C, almost without any side reactions.[20]

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[13] Johnson (to I. G. Farbenindustrie), British Patent 423,885 (1935).

[14] Graves: U. S. Patent 2,036,410 (1936).

[15] Seregienko: *Compt. rend. acad. sci. (U.S.S.R.)*, **26**, 69 (1940); *Chem. Abstracts*, **34**, 5419 (1940).

[16] Burgin, Groll and Roberts: *Refiner Natural Gasoline Mfr.*, October, 1938 (reprint).

[17] Sabatier and Senderens: *Compt. rend.*, **136**, 738, 921, 983 (1903).

[18] Rideal, E. K. and H. S. Taylor: *Catalysis in Theory and Practice*, London, Macmillan and Co., Ltd., 1919.

[19] Palmer and Constable: *Proc. Roy. Soc. (London)*, **98**, 13 (1920); **99**, 412 (1921); **101**, 175 (1922); **106**, 250 (1924); **107**, 255, 270 (1925); **108**, 355 (1925); **110**, 283 (1926) and **113**, 254 (1926).

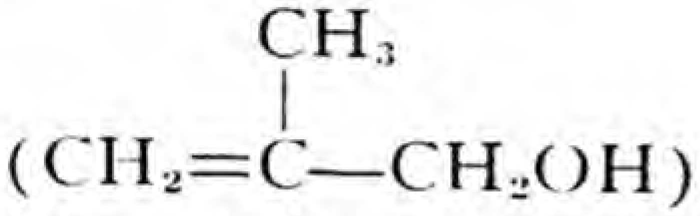
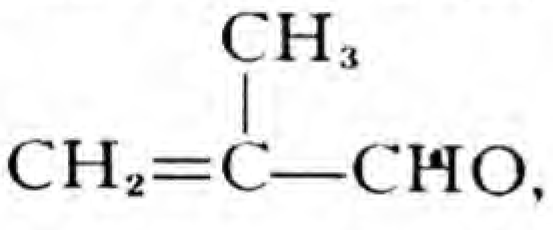
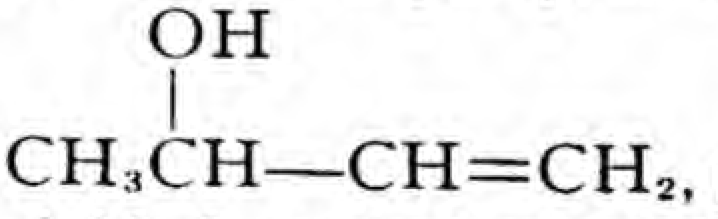
If nickel is used as catalyst for this reaction, further decomposition takes place:

$$CH_3CHO \rightarrow CH_4 + CO$$

The dehydrogenation of primary alcohols is a reversible process, the hydrogenation of the aliphatic aldehydes, in the presence of reduced nickel, proceeding rapidly at 180°C, and that of aromatic aldehydes below 230°C:[18]

$$R{\cdot}CH_2OH \rightleftarrows R{\cdot}CHO + H_2$$

Dehydrogenation of unsaturated primary and secondary alcohols to the corresponding unsaturated aldehydes and ketones has been studied by Groll:[20a]

1. Isobutenol,  $(CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_2OH)$, passed through a copper tube with brass spelter at 500°C yielded methyl acrolein,  $CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CHO$, the yield per pass being 38.6 per cent.
2. Butene-1-ol-3,  $CH_3\overset{\overset{\displaystyle OH}{|}}{C}H{-}CH{=}CH_2$, passed over the same catalyst at 550°C yielded methyl vinyl ketone, $CH_3COCH{=}CH_2$, the yield being 33 per cent.

Many other examples are cited. Other catalysts, e.g., copper, silver, zinc sulfide, etc. may be used, but brass is the best catalyst. Sulfur and halogen are poisons for this reaction, and it is suggested to pass the alcohols over metals such as can be used as catalysts at such low temperatures or at such high space velocities that no noticeable conversion to carbonyl compounds can take place.

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[20] Platonov and Anisimov: *J. Gen. Chem. (U.S.S.R.)*, **7**, 1360 (1937).
[20a] Groll: U. S. Patent 2,011,317 (1935).

At 400°C, in the presence of a catalyst, dehydration of the alcohol takes place, unsaturated hydrocarbons being formed:[18]

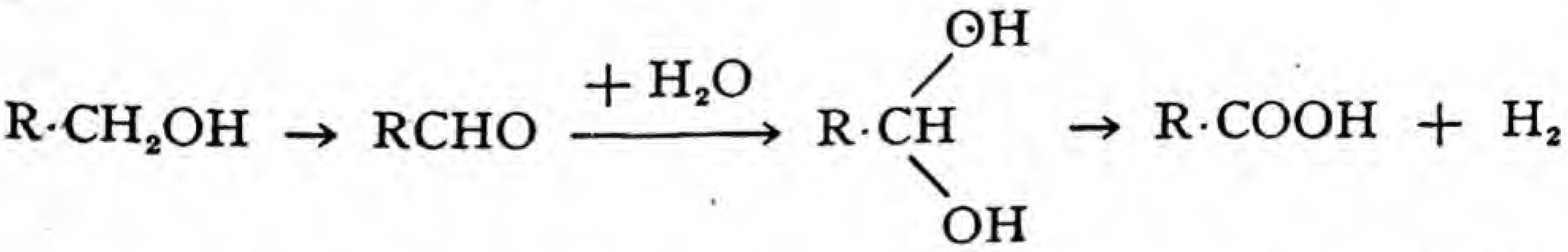
$$R{\cdot}CH_2{\cdot}CH_2OH \rightleftarrows R{\cdot}CH{=}CH_2 + H_2O$$

The oxides exert mixed action on alcohols, some being almost pure dehydrogenation catalysts: U_3O_8, MoO_3, V_2O_3, ZnO some are chiefly dehydration catalysts: Cr_2O_3 (colloidal), TiO_2, SiO_2 and some have mixed action: BeO, ZrO_2, Cr_2O_3 (calcined).[21]

The action of these catalysts on methyl alcohol is different from that on other alcohols, as dehydration is excluded. Sabatier presents the following data:[21]

Dehydrogenation	Partial decomposition	Almost complete decomposition
(CH_2O)	(CH_2O, CO, H_2)	(CO, H_2)
BeO	PbO	Fe_2O_3
SiO_2	Mo_2O_3	V_2O_5
TiO_2	CdO	SnO
ZnO		Light copper
ZrO_2		
MnO		
Al_2O_3		

It is claimed that organic acids can be formed directly from alcohols by double dehydrogenation of alcohols in the presence of water, using a copper catalyst to which small amounts of manganese and chromium are added:[22]



$$R{\cdot}CH_2OH \rightarrow RCHO \xrightarrow{+H_2O} R{\cdot}CH(OH)_2 \rightarrow R{\cdot}COOH + H_2$$

Using rhenium as a catalyst, ethyl, propyl, and butyl alcohols were dehydrogenated, the activity of the catalyst being of the same order as that of copper although at a somewhat higher temperature.[23]

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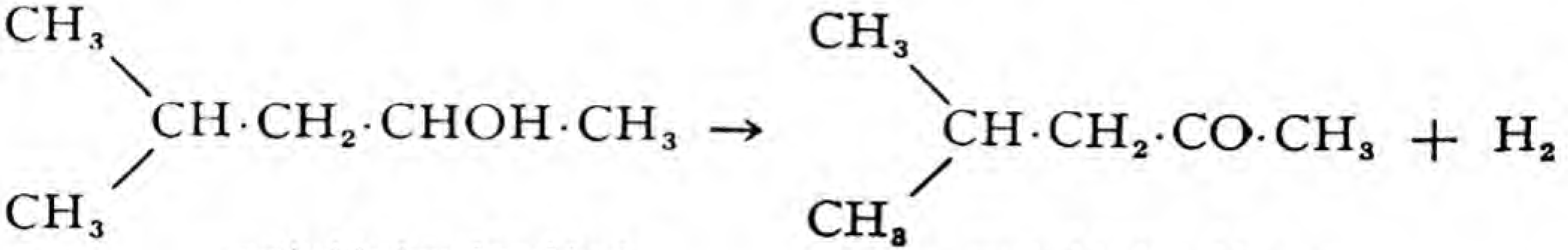
[21] Sabatier, P. and E. Emmett Reid: *Catalysis in Organic Chemistry*, New York, D. Van Nostrand Co., 1923, p. 674.

[22] Hale: U. S. Patents 2,027,377, and 2,027,378 (1936).

[23] Platonov, Anisimov, and Krasheninnkova: *Ber.*, **69 B**, 1050 (1936).

Secondary alcohols yield ketones when dehydrogenated. Ipatieff [24] passed isopropyl alcohol and methyl isobutyl carbinol through an iron tube at 600°C, and the alcohols decomposed chiefly into ketones and hydrogen:

$$\underset{\text{isopropyl alcohol}}{CH_3\cdot CHOH\cdot CH_3} \rightarrow \underset{\text{acetone}}{CH_3\cdot CO\cdot CH_3} + H_2$$



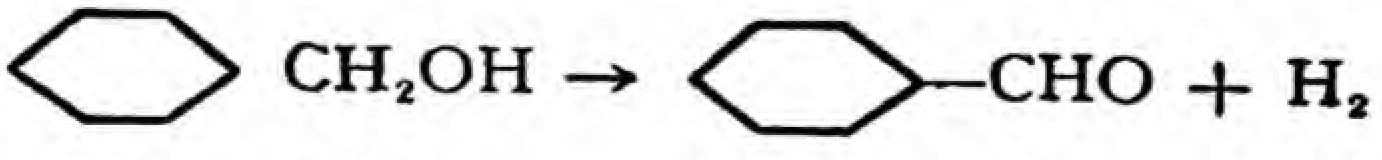
$$\underset{\text{methyl isobutyl carbinol}}{\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH\cdot CH_2\cdot CHOH\cdot CH_3} \rightarrow \underset{\text{methyl isobutyl ketone}}{\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH\cdot CH_2\cdot CO\cdot CH_3} + H_2$$

Ipatieff concludes from these experiments that catalytic decomposition of a secondary alcohol, in the presence of iron, may be used industrially for production of ketones. Almost quantitative yield of acetone was obtained by passing isopropyl alcohol through a glass or brass tube filled with brass filings and heated at 600 to 620°C.

Dehydrogenation of allyl alcohol, by passing it through brass filings, yielded acrolein as the chief product, accompanied by a small amount of divinyl (Ipatieff):

$$\underset{\text{allyl alcohol}}{CH_2{=}CH\cdot CH_2OH} \rightarrow \underset{\text{acrolein}}{CH_2{=}CH\cdot CHO} + H_2$$

Benzyl alcohol, passed through a copper tube heated up to 800°C, was dehydrogenated in the same way as an aliphatic alcohol, although under these conditions, part of the aldehyde was decomposed into benzene and carbon monoxide (Ipatieff):



benzyl alcohol benzaldehyde

Using brass filings, the dehydrogenation was effected at a lower temperature, and a good yield of the aldehyde was obtained.

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[24] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures*, New York, The Macmillan Company, 1937.

According to Ipatieff,[24, 25] if a metal catalyzes the aldehydic decomposition of alcohols, its oxide usually has the same property, even if it cannot be reduced completely to finely dispersed metal, zinc oxide being an example. Ipatieff states that the best catalysts for producing aldehydes and ketones from alcohols are zinc and brass, the best method being to fill brass tubes with brass filings.

According to Ipatieff,[24] it is assumed that very small amounts of water may alwavs be present in the decomposition of alcohols, and when this water comes into contact with a metal able to decompose it, it is decomposed into hydrogen and oxygen, the latter combining with the metal to form the corresponding oxide. If this oxide reduces easily, it will oxidize the alcohol into aldehyde with separation of water and regeneration of the metal, this cycle repeating itself indefinitely, while the metal actually remains unchanged:

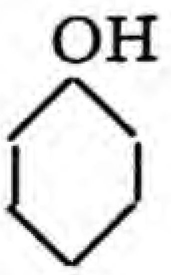
$$\text{Metal} + H_2O \rightarrow MeO + H_2$$

$$CH_3CH_2OH + MeO \rightarrow CH_3CHO + H_2O + Me$$

Under the action of a chromia catalyst, the aliphatic normal alcohols, containing six, seven or eight, carbon atoms, undergo a reaction of dehydrogenation and condensation of two molecules of alcohol to form a symmetrical ketone:[26]

$$2RCH_2CH_2OH \rightarrow RCH_2COCH_2R + CO + 3H_2$$

This reaction is supposed to consist of several steps: (1) Dehydrogenation to aldehyde; (2) aldol condensation; (3) removal of CO from the aldehyde group of the aldol, leaving a secondary alcohol; (4) dehydrogenation to ketone. At higher temperatures, a direct dehydrocyclization of the alcohols takes place with the formation of small amounts of phenols:

$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2OH \rightarrow$  $+ 4H_2$

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[25] Ipatieff: *Ber.*, 34, 596, 3579, 3585, 3589, 9596 (1901); *ibid.*, 35, 1047 (1902).

[26] Komarewsky and Coley: *J. Am. Chem. Soc.*, 63, 700 (1941).

GENERAL REFERENCE

Kassel: *J. Chem. Phys.*, **4**, 276, 438 (1936).

3. Cyclization (aromatization) and other ring closures

The formation of a closed ring structure such as from an aliphatic or olefinic compound, e.g., from acetylene with various compounds and a variety of other ring closures will be discussed here. The aromatization process of straight-chain hydrocarbons, and also some of the other ring closures, are dehydrogenation processes, and consequently dehydrogenation catalysts can be used, chromium oxide being an ideal cyclization catalyst.

Taylor and Turkevich [1a] have given a detailed account of the aromatization process which they summarize as consisting of the following single steps:

(1) Activated adsorption of the paraffin on to the surface of the catalyst
(2) Surface dehydrogenation with formation of adsorbed aromatic and adsorbed hydrogen
(3) Desorption of the hydrogen
(4) Desorption of the aromatic

The authors prepared chromic oxide gels by slow precipitation of dilute $Cr(NO_3)_3$ solutions with ammonia. N-heptane vapor was passed slowly over the catalyst at 470°C in a single pass and the conversion to toluene was measured, the data being as follows:

Catalyst	Temperature °C	Liquid flow cc/hr/15 g of catalyst	Mols. gas per mol. C_7H_{16}	Gas composition per cent hydrogen
Cr_2O_3	468	3	3.75	95
Cr_2O_3	468	9	3.77	94
Cr_2O_3	468	18	3.03	92
Cr_2O_3	468	27	2.75	98
ThO_2	468	3	0.05	1
Al_2O_3 (gel)	540	3	0.05	4
Al_2O_3 (activated)	540	3	0.4	42

Aromatic	Olefins	Saturated
100	0	0
100	0	0
92.3	1.8	5.9

The ThO_2 was deposited on pumice from $Th(NO_3)_4$, and the activated alumina was of high technical grade. Water vapor is a marked

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[1a] Taylor and Turkevich: *Trans. Faraday Soc.*, **35**, 921 (1939).

Liquid product per cent		
Aromatic	Olefins	Saturated
69	6	25
0	0.5	99.5
0	0.3	99.7
2	16.0	82

catalyst poison for chromic oxide on which it is strongly adsorbed. Oxygen also is a poison for this catalyst due to the fact that water is formed.

Hoog, Verheus and Zuiderweg [1b] studied cyclization of aliphatic hydrocarbons using tablets of Cr_2O_3 as catalyst which was slowly heated up to the working temperature, 465°C, in a current of hydrogen over a period of two hours, whereupon the hydrocarbon under test, in the vapor state, was passed over the catalyst tablets. It was found that all hydrocarbons, whose structure permits direct formation of a six-carbon ring, or which contains a six-carbon ring, are aromatized to a marked extent; but hydrocarbons whose structure does not allow of the direct formation of a six-carbon ring are not appreciably aromatized.

The aromatization increased in the order of the series: Paraffin $>$ corresponding aliphatic olefin $>$ corresponding six-ring naphthene $>$ corresponding cyclo-olefin. Within each of these hydrocarbon groups, aromatization increases with the number of carbon atoms in the molecule (C_6 to C_9). Branching of the carbon chain may either diminish or increase the suitability for aromatization. The aromatics formed in the cyclization of aliphatic hydrocarbons contain the shortest possible side chain or chains.

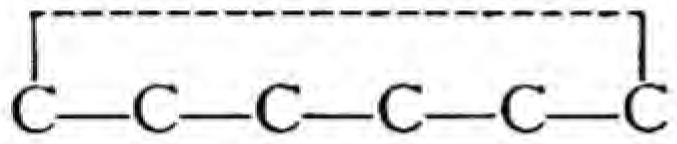
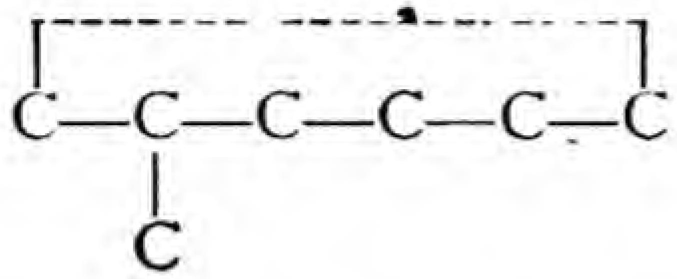
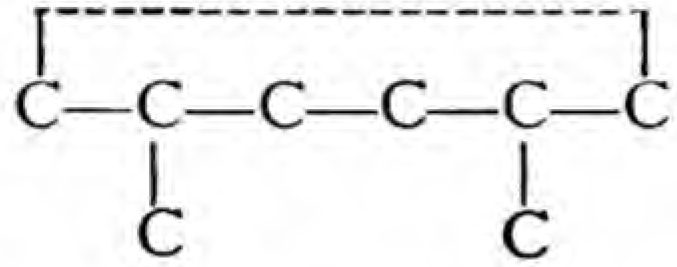
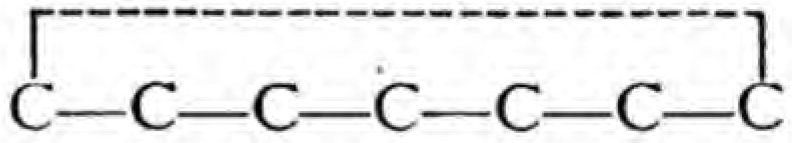
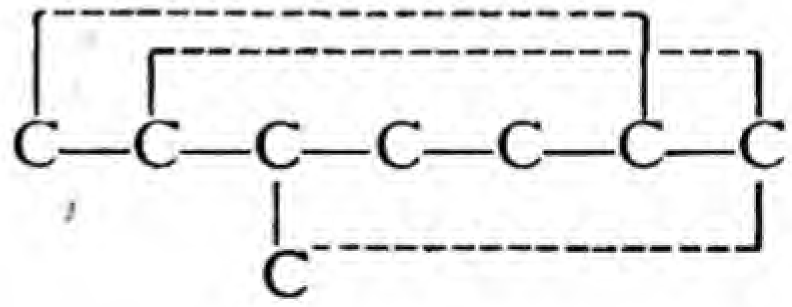
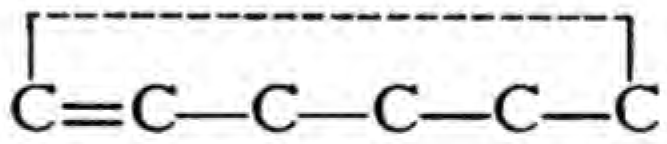
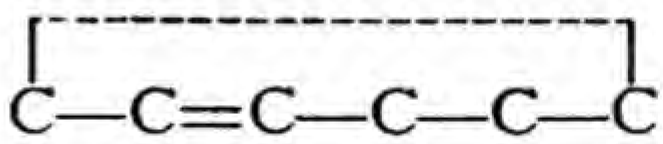
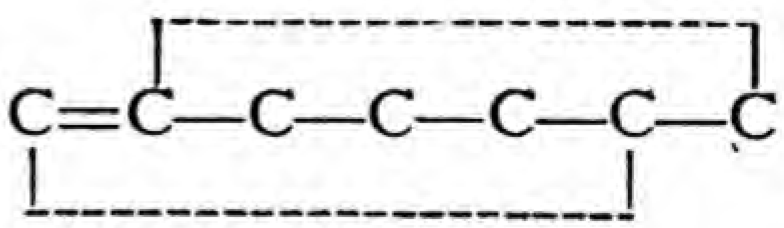
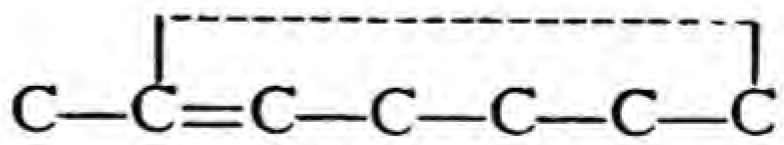
In the aromatization of the olefins, the degree of conversion may largely depend on the position of the double bond in the molecule.

The aromatization reaction proceeds as simple ring closure, without isomerization of the carbon skeleton; secondary carbon atoms preferentially participate in the ring closure. The olefins present in the reaction products, under the conditions of this work, invariably contained a centrally situated double bond, this being due to the fact that the chromium oxide catalyzed the shift of the double bond in an olefin to a more central position.

The following two tables give an illustration of this important process suitable to convert synthetically straight-chain petroleum hydrocarbons to aromatics.

[1b] Hoog, Verheus and Zuiderweg: *Trans. Faraday Soc.*, **35**, 993 (1939).

THE INFLUENCE OF STRUCTURE ON AROMATIZATION OF HYDROCARBONS

Paraffin	Reaction	Aromatization (per cent)	
n-hexane		19½	
2-methyl hexane		31	
2,5-dimethyl hexane		52	
n-heptane		36	
3-methyl heptane		35	
n-hexene-1	 *	31	30
n-hexene-2		18	15
n-heptene-1		69	22
n-heptene-2		65	24

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* This reaction possibility is not realized.

IDENTIFICATIONS OF THE AROMATICS FORMED

Base material	Aromatics which can be formed by direct ring closure	Individual aromatics experimentally identified
n-hexane	benzene	$\sim$100 per cent benzene[a•]
n-heptane	toluene	$>$ 95 per cent C_7-aromatic[•] (toluene)[a•]
2-methyl hexane	toluene	$\sim$ 100 per cent toluene[a•]
n-octane	ethyl benzene o-xylene	$>$ 95 per cent C_8-aromatic[a•] of which $>$ 80 per cent o-xylene[•]
3-methyl heptane	ethyl benzene o-xylene p-xylene	$\sim$ 100 per cent C_8-aromatic[a] of which 5 per cent ethyl benzene[c] 35 per cent o-xylene 5 per cent m-xylene 55 per cent p-xylene
2, 5-dimethyl hexane	p-xylene	$\sim$ 100 per cent C_8-aromatic[a] of which $>$ 80 per cent p-xylene[d•] of
n-nonane	n-propyl benzene o-methyl ethyl benzene	$\sim$ 80 per cent C_9-aromatic[a•] of which $>$ 90 per cent o-methyl ethyl benzene[c]

[a] Quantities estimated from distillation data, etc.
[b] Identified by and estimated from nitration and bromination results.
[c] Identified by and estimated from oxidation experiments carried out according to *Moldawsky (J. Gen. Chem. (U.S.S.R.),* 7, 169, 1937).
[d] Identified by and estimated from results of a nitration experiment carried out according to *Reichel (Chem. Z.,* 55, 744, 1931).
[e] Remainder: Lower-molecular-weight aromatics.
[•] These results fully confirm those of *Moldawsky* and others.

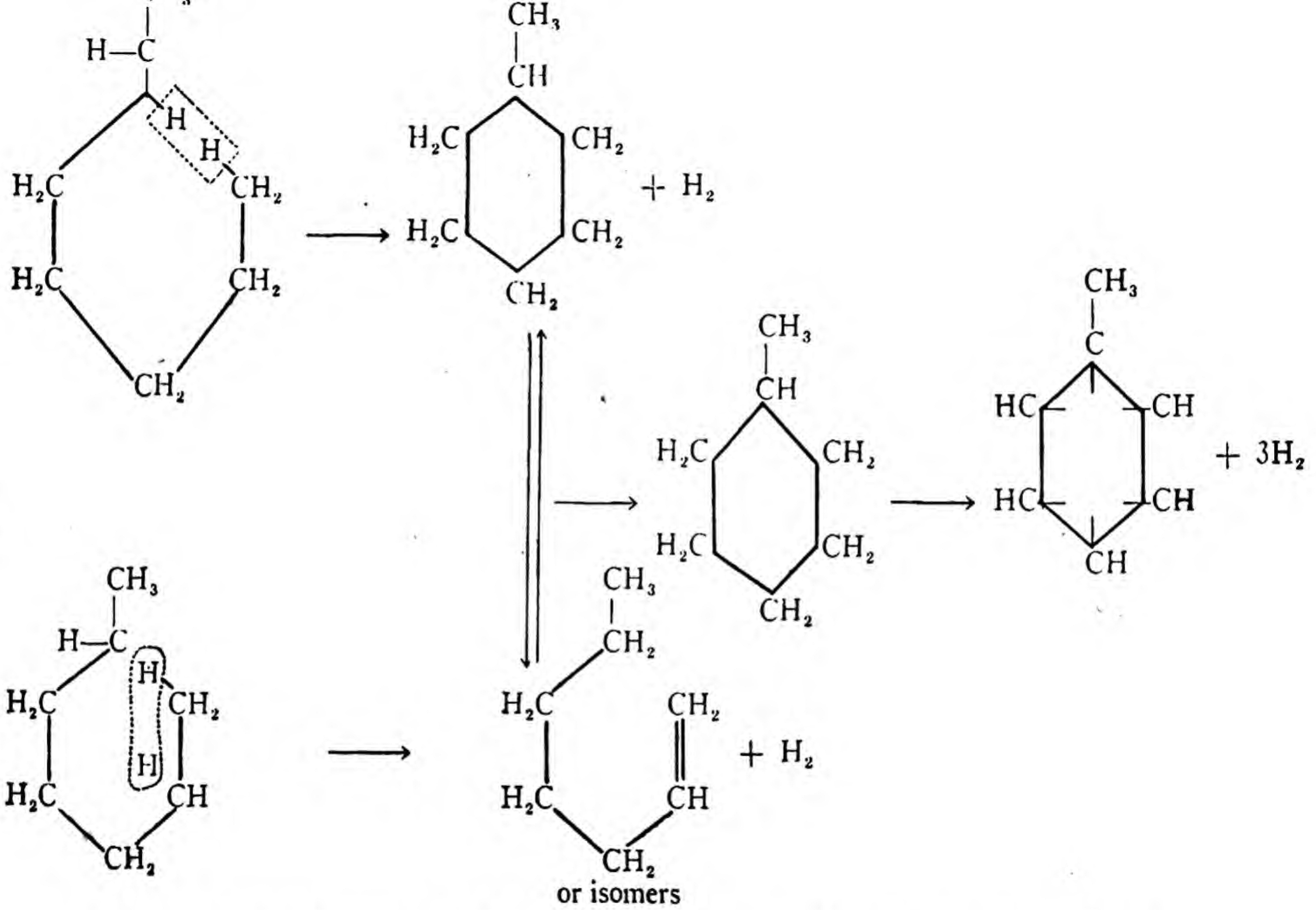
Grosse, Morrell, and Mattox[1c] term the ring-closure dehydrocyclization, the conversion of n-heptane being presented as follows:

n-Heptane was converted into toluene with a yield of 0.75 mol toluene per mol of n-heptane (75% yield) in one pass, and with over 90% yield by recycling (see p. 116).

The catalysts used consisted of minor molar proportions of oxides of the transition metals of the sixth (e.g., Cr or Mo), fifth (e.g., V), and fourth (e.g., Ti or Ce) groups of the periodic system supported on carriers of relatively low catalytic activity such as alumina or magnesia. Other carriers, which do not give unfavorable reaction with metal oxides and which possess a stable and large surface, may also be used. The dehydrogenation metal compounds may be deposited upon the carriers from aqueous or other solutions, or they may simply be mechanically mixed with the carriers in wet or dry condition.

These investigators cyclicized a large number of pure aliphatic hydrocarbons using different catalysts under varying conditions, specific examples being listed on p. 217.

[1c] Grosse, Morrell and Mattox: *Ind. Eng. Chem.,* 32, 528, 1940.



n-heptane ⟶ intermediate stage (radical or olefin) ⟶ cyclohexane ⟶ toluene

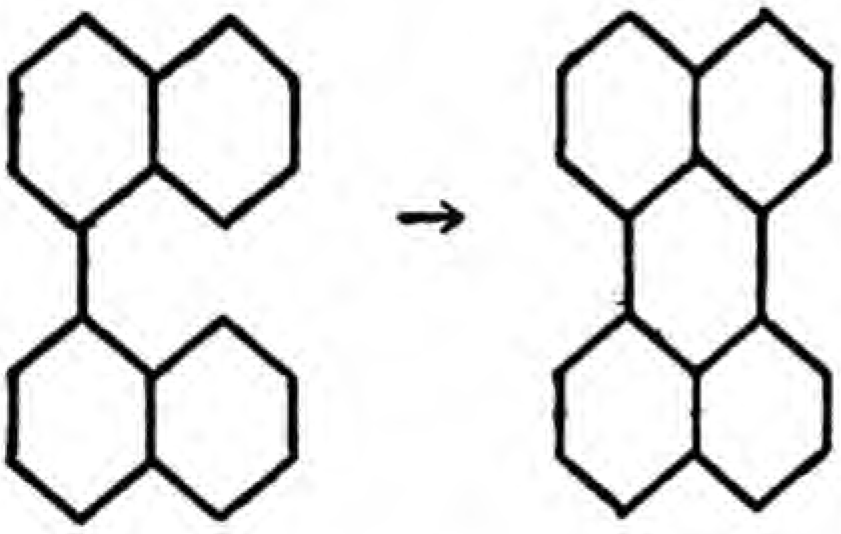
C_7H_{16} ⟶ $C_7H_{14} + H_2$ ⟶ C_7H_{14} ⟶ $C_7H_8 + 3H_2$

n-hexanes → benzene
n-hexenes → benzene
n-heptanes → toluenes
n-heptenes → toluenes

$$\left.\begin{array}{l}\text{n octanes}\\ \text{n-octenes}\end{array}\right\}\longrightarrow \begin{array}{l}\text{o-, m-, and p-xylenes,}\\ \text{and ethylbenzene}\end{array}$$

The rate of cyclization can be measured by the rate of evolution of hydrogen as it has been done by Kazanskii and Liberman,[2] who found that isobutane was aromatized over platinized carbon with a mean apparent energy of activation of 15,930 to 16,350 calories per mol, the energy of activation of aromatization of cyclohexane over the same catalyst being 16,070 calories per mol.

Using aluminum chloride as a catalyst between 80° and 140°C, α-dinaphthyl yields perylene by dehydrogenation:[3]



Acetylene forms ring structures with different compounds by elimination of hydrogen at 300°C, in the presence of several metallic oxides, viz., anhydrous alumina, iron oxide, chromium sesquioxide, thoria, titanium oxide:[4]

$$2CH{\equiv}CH + NH_3 \rightarrow \underset{\text{pyrrol}}{C_4H_5N} + H_2$$

$$3CH{\equiv}CH + NH_3 \rightarrow \underset{\text{picoline}}{C_6H_7N} + H_2$$

---

[2] Kazanskii and Liberman: *J. Gen. Chem. (U.S.S.R.)*, **9**, 1431 (1939); *Chem. Abstracts*, **34**, 1544 (1940).

[3] Scholl, Seer, and Weltzenbock: *Ber.*, **43**, 2203 (1910).

[4] Sabatier, P.: *La Catalyse en Chemie Organique*, Paris, Librairie Polytechnique, 1920; P. Sabatier and E. Emmett Reid: *Catalysis in Organic Chemistry*, New York, D. Van Nostrand Co., 1923.

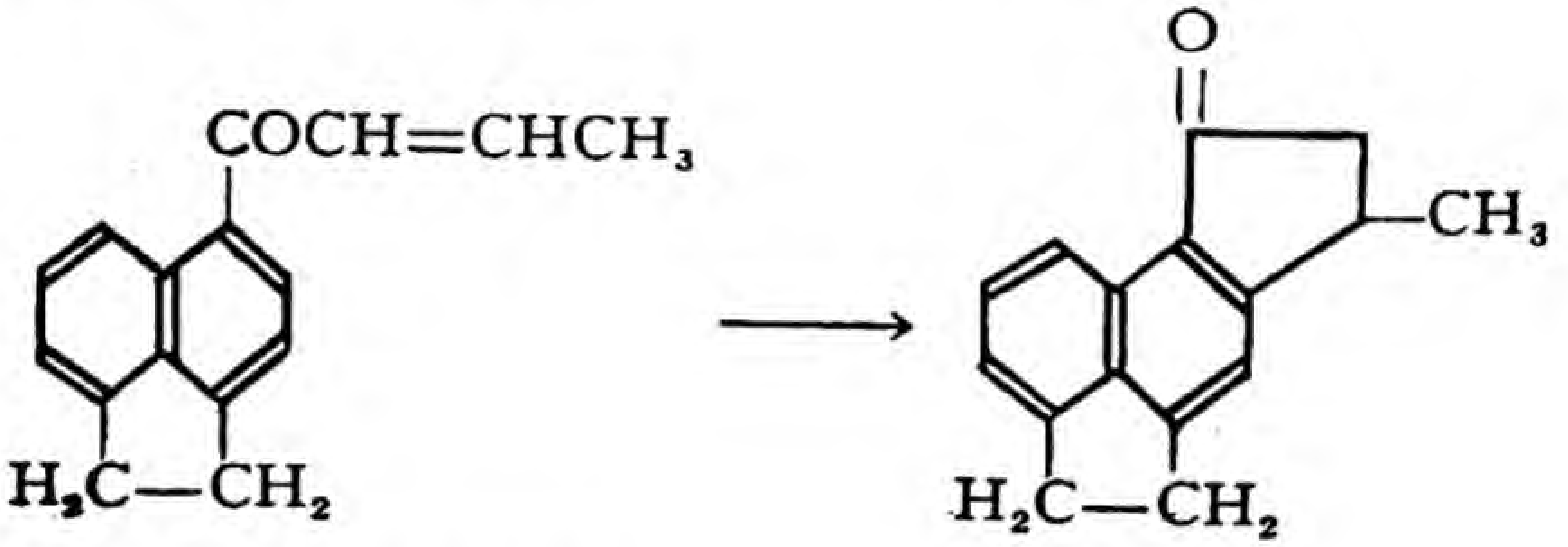
$$4CH{\equiv}CH + NH_3 \rightarrow \underset{\text{collidine}}{C_8H_{11}N}$$

$$2CH{\equiv}CH + H_2S \rightarrow \underset{\text{thiophene}}{C_4H_4S} + H_2$$

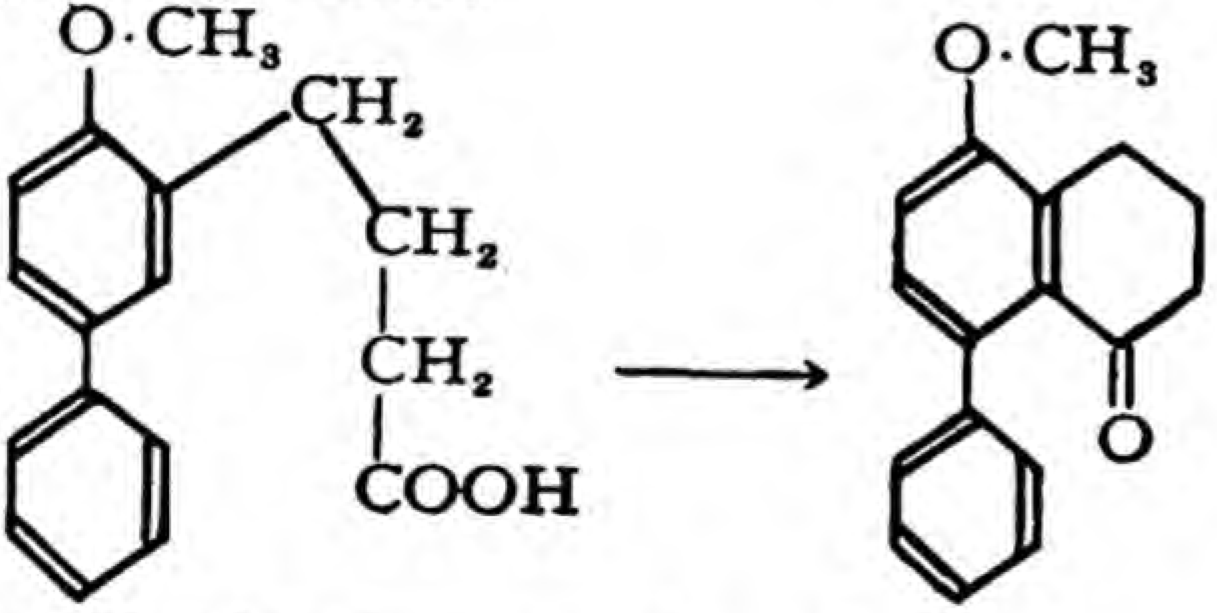
$$2CH{\equiv}CH + H_2O \rightarrow \underset{\text{furfurane}}{C_4H_4O} + H_2$$

Ethylene reacts in an analogous manner at higher temperatures. Hydrogen fluoride causes several ring closures:[5, 6, 7]

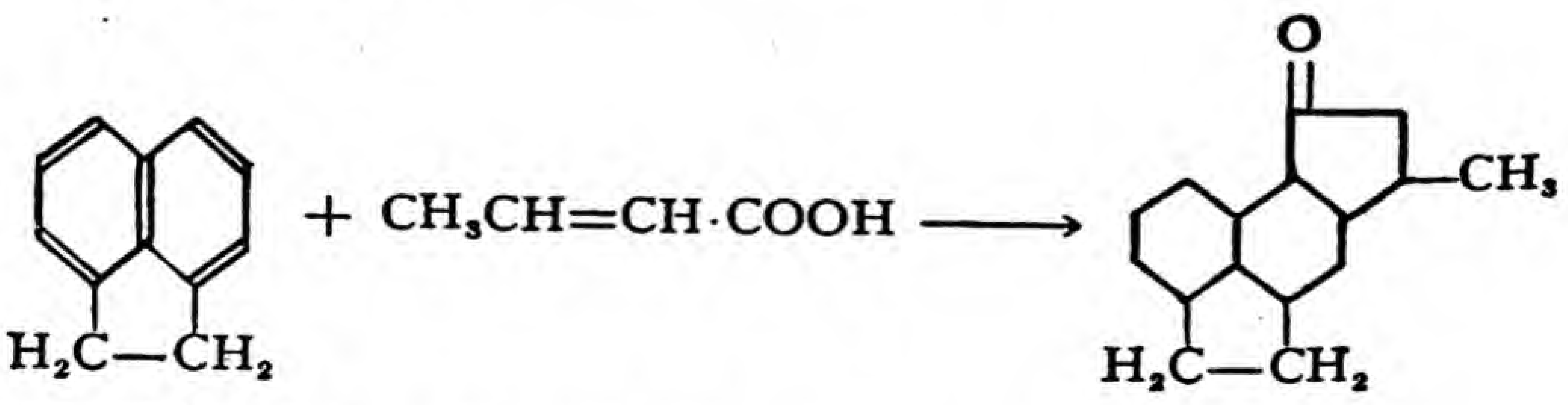
(1) Olefin group reacts:


COCH=CHCH₃
H₂C—CH₂
O
CH₃
H₂C—CH₂

(2) Carboxyl group reacts:


O·CH₃
CH₂
CH₂
CH₂
COOH
O·CH₃
O

(3) Compound having two reactive groups reacts with aromatic compound:


H₂C—CH₂
+ CH₃CH=CH·COOH
O
CH₃
H₂C—CH₂

---

[5] Simons: *Ind. Eng. Chem.*, **32**, 178 (1940).

[6] Calcott, Tinker, and Weinmayer: *J. Am. Chem. Soc.*, **61**, 949 (1939).

[7] Simons and Archer: *Ibid.*, **61**, 1521 (1929).

4. Hydrogenation

By catalytic hydrogenation is understood the chemical addition of hydrogen to a compound in the presence of a catalyst. By this process, carbon, nitrogen, sulfur, and halogens may be eliminated from a compound as methane, ammonia, hydrogen sulfide, and hydrogen halides, respectively. The substance to be hydrogenated is brought into contact with finely divided metals, oxides, or a fixed catalytic surface, and hydrogen at a proper temperature.

Catalytic hydrogenation has been described in detail by Sabatier,[1] Ipatieff,[2] Adkins,[3] Fenske,[4] Linstead,[5] Bergius,[6, 7] and in a recent symposium on hydrogenation in Industrial and Engineering Chemistry.[8] Numerous compounds have been hydrogenated, but only a few typical examples can be mentioned here.

According to Adkins,[3] a good catalyst for hydrogenation must fulfil the following requirements: It must

(1) be stable in the presence of the reactants
(2) adsorb and activate hydrogen
(3) adsorb and activate the hydrogen acceptor
(4) hold the activated hydrogen and hydrogen acceptor in the proper relationship for reaction
(5) desorb or set free the reaction product(s)

Adkins points out that the catalyst, used in hydrogenation, combines with both the hydrogen acceptor and the hydrogen, and that each is activated and held in such a position with respect to the other that reaction may ensue.

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[1] Sabatier, P.: *La Catalyse en Chimie Organique.* Paris, Librairie Polytechnic, 1920; P. Sabatier and E. Emmett Reid: *Catalysis in Organic Chemistry,* New York, D. Van Nostrand Co., 1923.

[2] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures,* New York, The Macmillan Company, 1937.

[3] Adkins, H.: *Reactions of Hydrogen with Organic Compounds over Copper Chromium Oxide and Nickel Catalysts,* Madison, The University of Wisconsin Press, 1937.

[4] Fenske, M. R.: Hydrogenation. Chapter VIII of Groggins' *Unit Processes in Organic Synthesis,* New York, McGraw-Hill Book Co., Inc., 1938.

[5] Linstead et al.: *J. Am. Chem. Soc.,* **64,** 1985, 1991, 2003, 2006, 2009, 2014, 2002 (1942).

[6] Bergius: *Z. angew. Chem.,* **25,** 1171 (1912).

[7] Bergius, F.: *An Historical Account of Hydrogenation,* Proc. World Petroleum Congress, 1933.

[8] Symposium: *Ind. Eng. Chem.,* **32,** 1189 (1940).

Adkins[8a] also concludes that the rate of hydrogenation over a catalyst is dependent on the following factors:

(1) acceptor of hydrogen
(2) impurities in the acceptor
(3) temperature during the hydrogenation
(4) pressure of hydrogen
(5) amount of solvent
(6) kind of solvent
(7) amount of catalyst
(8) ratio of catalyst to hydrogen acceptor
(9) time
(10) temperature involved in all stages of the hydrogenation experiment
(11) thoroughness of the mixing of the hydrogen acceptor, catalyst, and hydrogen

To these factors should be added (12) the activity of the catalyst, and (13) selectivity of same, two factors which probably were almost constant in Adkins' experiments, but which vary considerably in hydrogenations, in general. Also, the solubility of the hydrogen in the reaction medium is a matter of considerable importance, undoubtedly more so than it is generally realized. Some data, presenting the solubility of hydrogen in n-butane at different temperatures and pressures, are as follows:[9]

Temperature, °C	Pressure, atm. abs.	Mol per cent Liquid phase	Mol per cent Vapor phase
23.9	22.2	2.0	83.2
	78.6	6.2	—
	103.0	7.4	—
82.2	42.6	4.0	62.7
	60.8	6.3	—
	69.0	7.0	—

[8a] Adkins, H.: *Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts,* Madison, The University of Wisconsin Press, 1937, p. 9.

[9] Nelson and Bonnel: *Ind. Eng. Chem.,* **35, 204** (1943).

Temperature, °C	Pressure, atm. abs.	Mol per cent	
		Liquid phase	Vapor phase
	93.6	9.9	83.3
	105.8	11.1	—
115.6	38.6	3.2	—
	48.9	5.1	42.0
	65.9	7.5	—
	71.0	8.3	—
	91.8	11.1	62.4

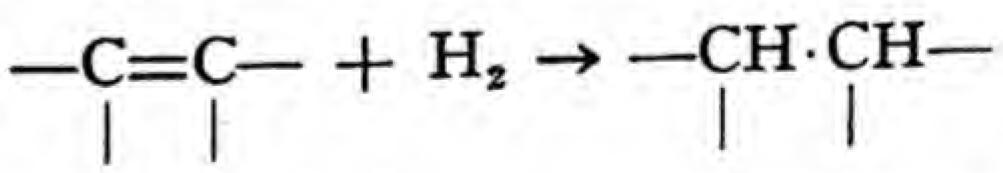
Hydrogenation reactions being so numerous, it is difficult to make a brief classification of the typical reactions, although this would be useful for comprehension of the underlying principles.

Sabatier[1] set up the followinng four classes:

(1) Simple reductions without fixation of hydrogen
(2) Reductions with simultaneous fixation of hydrogen
(3) Fixation of hydrogen by addition to molecules with multiple bonds
(4) Hydrogenation accompanied by rupture of the molecule

In this discussion, we shall follow Adkins'[3] classification * as it is uniformly tested, and wide enough to cover the problem of hydrogenation in this book. As Adkins' work refers to two catalysts only, some works supplementing that of Adkins' et al. are added.

1. Hydrogenation of double bonds between two carbon atoms:



$$-\underset{|}{C}=\underset{|}{C}- + H_2 \rightarrow -\underset{|}{C}H\cdot\underset{|}{C}H-$$

Adkins terms this bond the alkene linkage, and assumes that with Raney nickel, the majority of these linkages will be hydrogenated at 100°C and 100 atmospheres of pressure, although for rubber, a hydrogenation temperature of 250 to 275°C is required. Copper-chromium oxide is equally active only at higher temperatures, 100 to 175°C.

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* By permission of Professor H. Adkins, University of Wisconsin, and the University of Wisconsin Press.

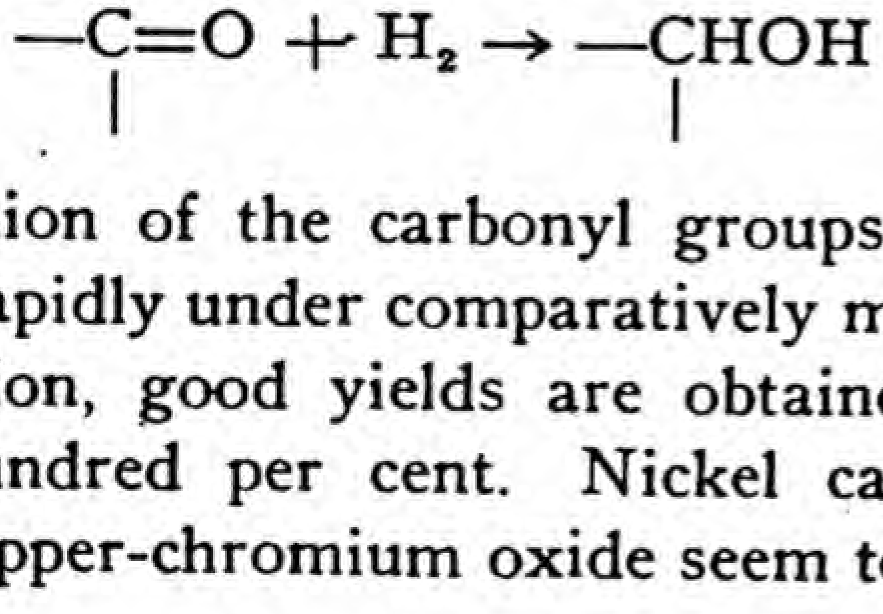
Ethylene, $CH_2=CH_2$, is readily hydrogenated to ethane, $CH_3 \cdot CH_3$, in the presence of nickel,[10,11] cobalt,[12] copper,[13] iron,[14] colloidal platinum,[15] etc. The ethylene linkage, in aromatic side chains, is also readily hydrogenated; styrene, $C_6H_5 \cdot CH=CH_2$, for example, yields ethylbenzene, $C_6H_5 \cdot CH_2 \cdot CH_3$, upon hydrogenation with nickel, the aromatic nucleus not being hydrogenated under such conditions. Stilbene, $C_6H_5 \cdot CH=CH \cdot C_6H_5$, which contains two aromatic nuclei linked by an ethylenoid linkage, is readily hydrogenated to dibenzyl, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$, over nickel at 240°C.[16] Allyl alcohol, $CH_2=CH \cdot CH_2OH$, is hydrogenated to propyl alcohol over nickel at 130–170°C.[17]

2. *Hydrogenation of triple bonds between two carbon atoms:*

The best studied reaction of this type is the hydrogenation of acetylene by various catalysts and temperatures: Platinum metals mixed with base metal at 100°C;[18] palladium on silica gel;[19] nickel;[19a] iron prepared from $FeAl_3$, which hydrogenates to ethylene only.[19a] The reaction of hydrogenating acetylene to ethane is accompanied with a considerable contraction of volume:

$$CH \equiv CH + 2H_2 \rightarrow CH_3 \cdot CH_3$$

3. *Hydrogenation of carbonyls:*



$$\underset{|}{—C}=O + H_2 \rightarrow \underset{|}{—C}HOH$$

The hydrogenation of the carbonyl groups in aldehydes and ketones proceeds rapidly under comparatively mild conditions and, by proper regulation, good yields are obtained, in many cases practically one hundred per cent. Nickel catalysts of various preparation and copper-chromium oxide seem to be effective.

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[10] Kather and Reid: *J. Am. Chem. Soc.*, **37**, 2115 (1915).

[11] Sabatier and Senderens: *Compt. rend.*, **124**, 1359 (1897).

[12] German Patent 262,541 (1910).

[13] Pease: *J. Am. Chem. Soc.*, **45**, 1196 (1923); Pease and Harris: *Ibid.*, **49**, 2503 (1927).

[14] Hansford and Emmett: *J. Am. Chem. Soc.*, **60**, 1185 (1938).

[15] Skita and Meyer: *Ber.*, **45**, 3879 (1912).

[16] Sabatier and Murat: *Ann. chim.* (9) **4**, 284 (1915).

[17] Sabatier: *Compt. rend.*, **144**, 879 (1907).

[18] German Patent 339,493 (1921).

[19] Morris and Reyerson: *J. Phys. Chem.*, **31**, 1332 (1927).

[19a] Paul and Hilly: *Compt. rend.*, **206**, 608 (1938).

Acetone, $CH_3 \cdot CO \cdot CH_3$ is quantitatively converted into propanol-2, $CH_3CH(OH)CH_3$, by hydrogenation with nickel on kieselguhr,[20] Raney nickel,[21] and copper-chromite catalysts.[8] Benzaldehyde, $C_6H_5 \cdot CHO$, is converted into benzyl alcohol, $C_6H_5 \cdot CH_2OH$;[22] and furfural, $C_4H_3O \cdot CHO$, into furfuryl alcohol, $C_4H_3O \cdot CH_2OH$, using copper-chromite catalyst.[23] Fructose, dissolved in water, is almost quantitatively hydrogenated to mannitol at 150°C using nickel on kieselguhr as catalyst. Glucose, dissolved in water or alcohol, is converted into sorbitol, when hydrogenated over nickel on kieselguhr or copper-chromium oxide at 150°C and 160°C respectively.

An interesting reaction is the hydrogenation of carbon dioxide in the presence of an amine when the formate of the amine is formed, at a temperature of 80°C, or less over Raney nickel:[8, 24]

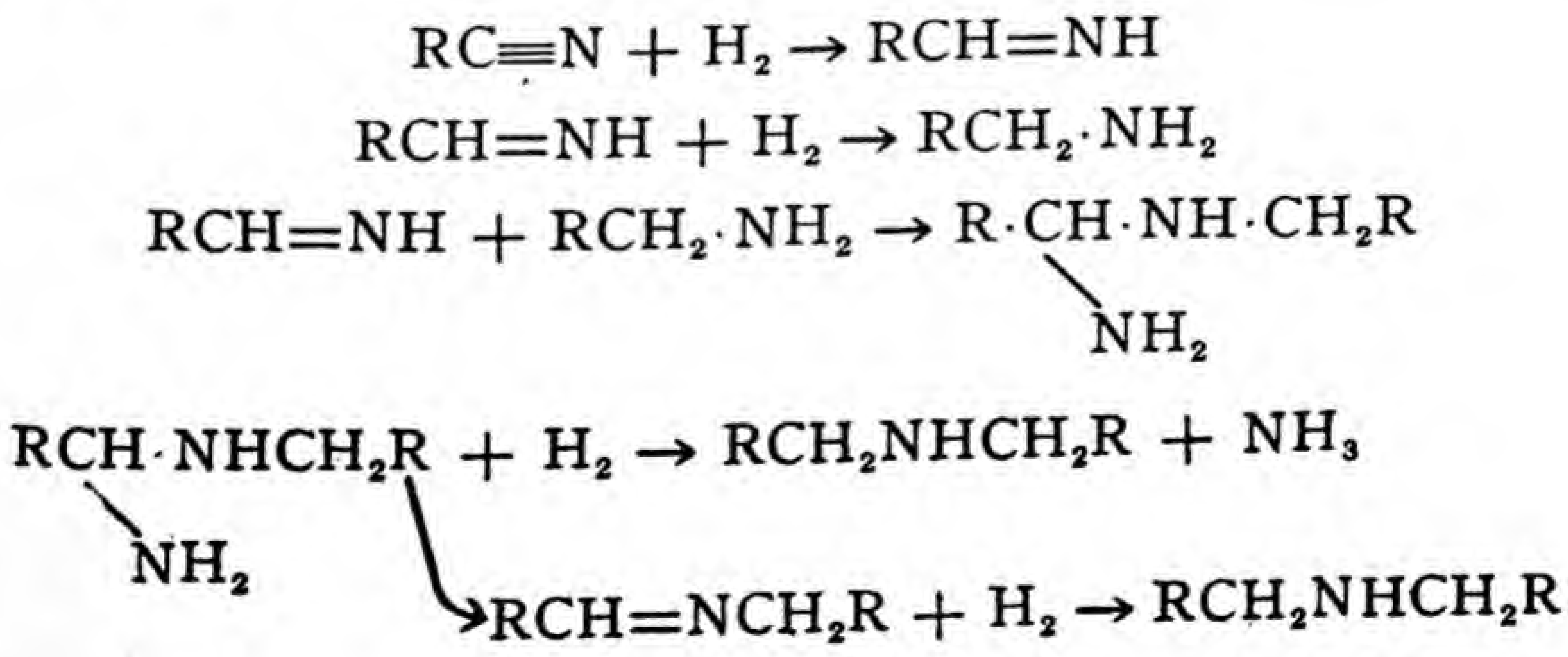
$$CO_2 + H_2 \rightarrow HCOOH$$

$$HCOOH + RNH_2 \rightarrow HCOO \cdot NH_3 \cdot R$$

4. Hydrogenation of cyanides:

$$RCN + 2H_2 \rightarrow RCH_2NH_2$$

When nickel is used as catalyst for this reaction, side reactions take place which lead to the formation of secondary amines, especially if the reaction is not carried out rapidly:



$$RC{\equiv}N + H_2 \rightarrow RCH{=}NH$$

$$RCH{=}NH + H_2 \rightarrow RCH_2 \cdot NH_2$$

$$RCH{=}NH + RCH_2 \cdot NH_2 \rightarrow R \cdot \underset{\diagdown NH_2}{CH} \cdot NH \cdot CH_2R$$

$$\underset{\diagdown NH_2}{RCH} \cdot NHCH_2R + H_2 \rightarrow RCH_2NHCH_2R + NH_3$$

$$\searrow RCH{=}NCH_2R + H_2 \rightarrow RCH_2NHCH_2R$$

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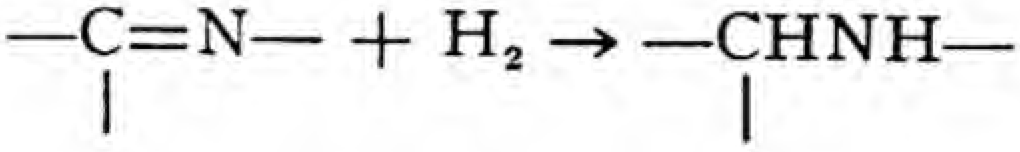
[20] Adkins and Zartman: *J. Am. Chem. Soc.*, **54**, 1668 (1932).
[21] Adkins and Covert: *Ibid.*, **54**, 4116 (1932).
[22] Adkins and Connor: *Ibid.*, **53**, 1091 (1931).
[23] Adkins and Covert: *Ibid.*, **59**, 135 (1937).
[24] Adkins and Farlow: *Ibid.*, **57**, 2222 (1935).

These side reactions are avoided if Adams' platinum catalyst is used and the reaction is carried out in acetic anhydride, which prevents the interaction with the imine by acetylating the primary amine.[3, 25, 26]

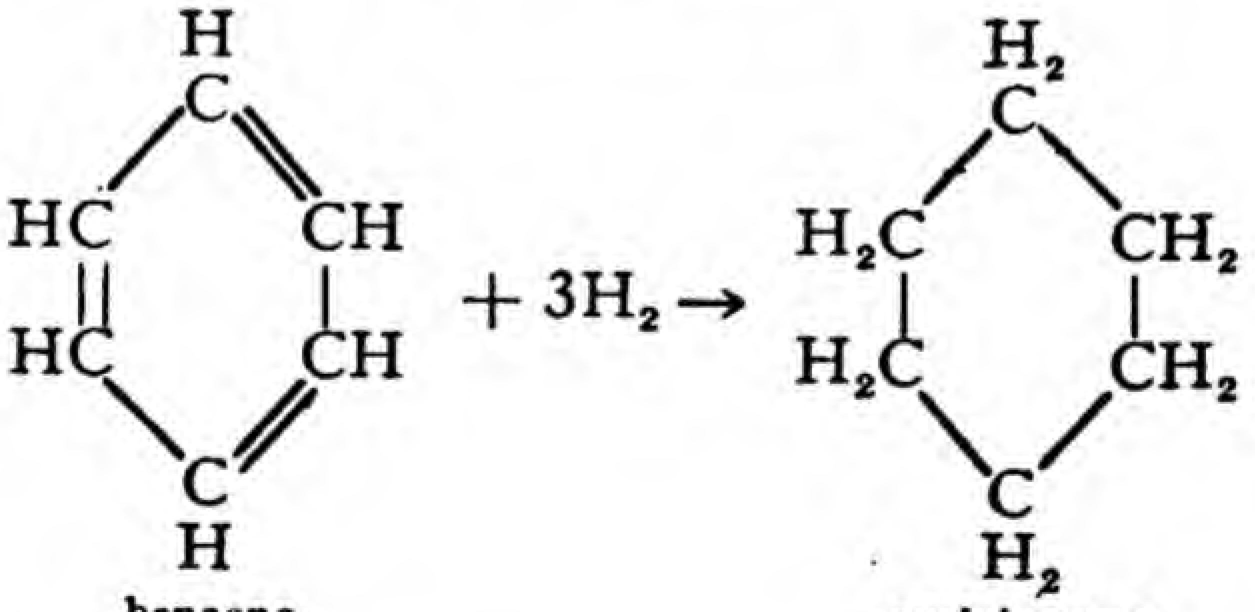
5. *Hydrogenation of imines:*



$$-\underset{|}{C}{=}N- + H_2 \rightarrow -\underset{|}{C}HNH-$$

With Raney nickel imines are rapidly hydrogenated at a temperature below 80°C. The unsubstituted imines yield a mixture of primary and secondary amines due to the reaction of imine with amine as in the case of the hydrogenation of cyanides.[3, 27]

6. *Hydrogenation of the benzenoid nucleus:*



benzene cyclohexane

Hydrogenation of the benzene nucleus has always been a rather difficult operation, and the discovery that this reduction could be accomplished by hydrogenating over nickel is very important from the standpoint of organic synthesis.

Sabatier and Senderens found[28] that benzene was directly hydrogenated to cyclohexane at temperatures over 70°C, and the maximum velocity of the reaction was between 170 and 190°C

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[25] Frebault: *Compt. rend.*, **140**, 1036 (1905).

[26] Sabatier and Senderens: *Ibid.*, **140**, 482 (1905).

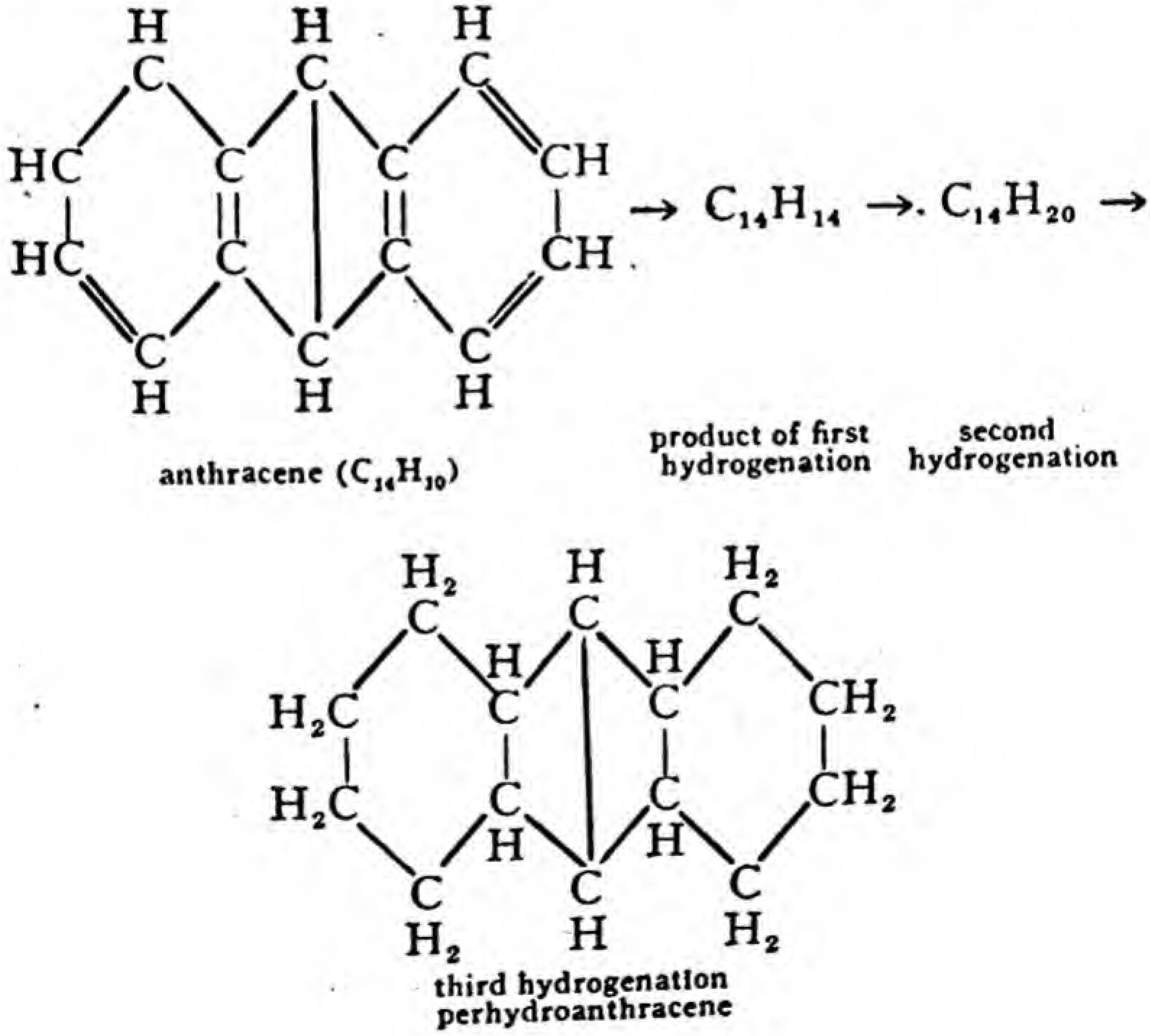
[27] Winans and Adkins: *J. Am. Chem. Soc.*, **55**, 2051 (1933).

[28] Sabatier and Senderens: *Compt. rend.*, **132**, 210 (1901).

when reduced nickel was used as catalyst. At higher temperatures, above 300°C, some methane is formed and carbon deposits on the nickel.

Styrene, $C_6H_5 \cdot CH{=}CH_2$, was hydrogenated at 160°C over very active nickel to ethylcyclohexane, $C_6H_{11} \cdot CH_2 \cdot CH_3$; but if a less active nickel was used, toward 200°C, practically no ethylbenzene, $C_6H_5 \cdot CH_2 \cdot CH_3$, was obtained.

Ipatieff and collaborators[29, 30] used nickel oxide catalyst and high pressures and temperatures in aromatic hydrogenations. Anthracene, $C_6H_4{=}(CH)_2{=}C_6H_4$, was hydrogenated at a hydrogen pressure of 100 to 125 atmospheres, and at temperatures from 260 to 270°C. 2 grams of nickel oxide was used to hydrogenate 25 grams of anthracene. It was necessary to repeat the hydrogenation three times in order to obtain saturation:


→ $C_{14}H_{14}$ → $C_{14}H_{20}$ →
anthracene ($C_{14}H_{10}$)
product of first hydrogenation
second hydrogenation
third hydrogenation
perhydroanthracene

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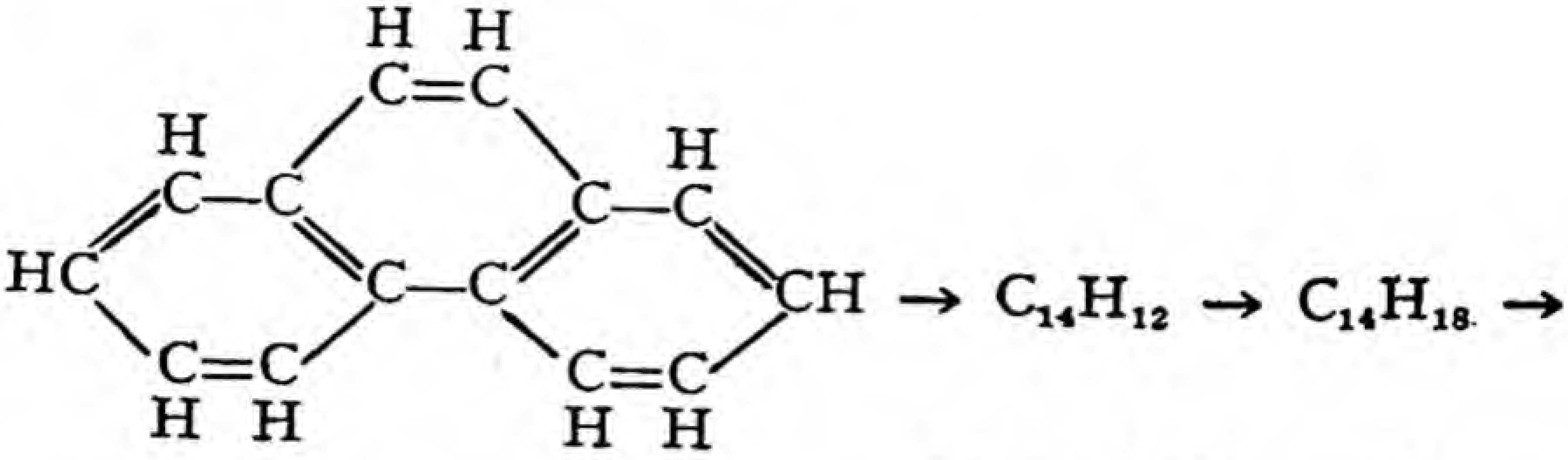
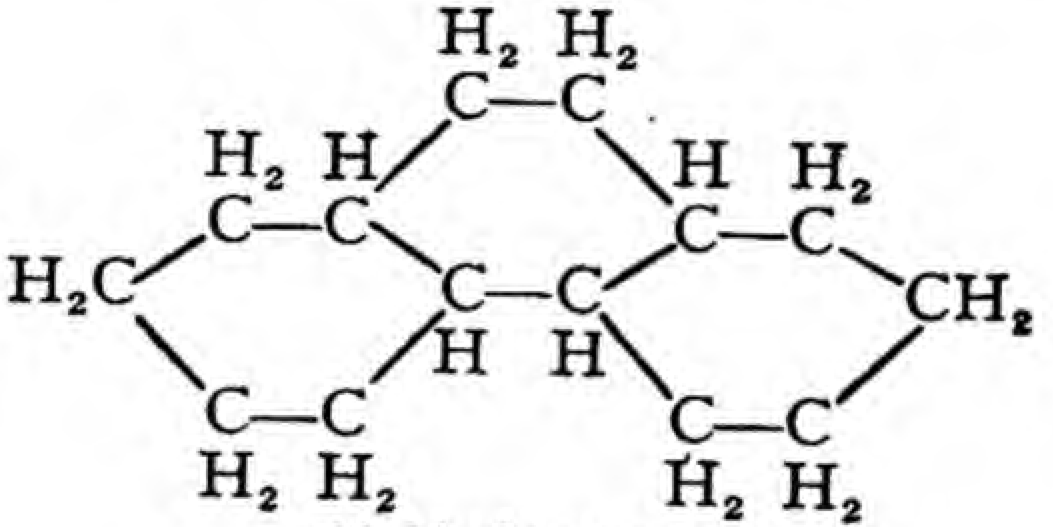
[29] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures*, New York, The Macmillan Co., 1937, p. 217.

[30] Ipatieff, Jakowlew, and Rakitin: *Ber.*, 41, 996 (1908).

Phenanthrene, $C_{14}H_{10}$, was hydrogenated by the same method at 400°C, and also here triple hydrogenation was required in order to obtain a fully saturated product:



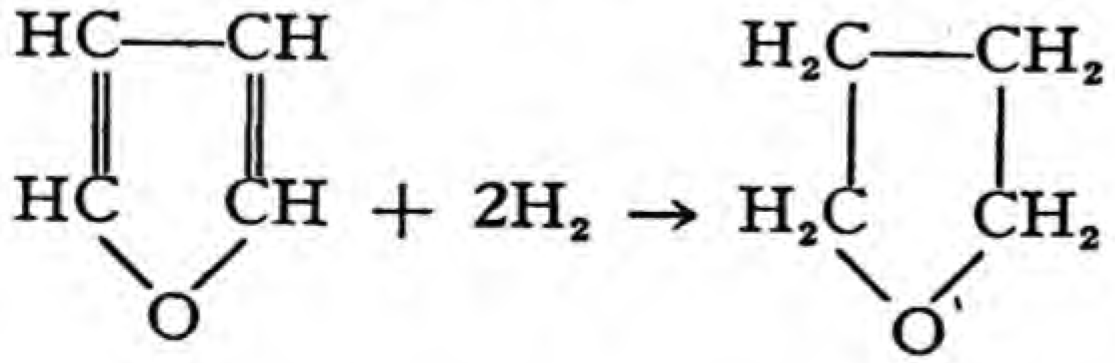
phenanthrene ($C_{14}H_{10}$) product of first hydrogenation second hydrogenation



third hydrogenation, perhydrophenanthrene ($C_{14}H_{24}$)

Adkins[31] and his collaborators have carried out a very large number of hydrogenation of aromatic compounds using nickel on kieselguhr and Raney nickel as catalysts. This investigation included alkyl benzenes, aromatic methanes and ethanes, diphenyl derivatives, phenols, aromatic alcohols, ethers, esters, amines, and other aromatic compounds.

7. Hydrogenation of the furanoid nucleus:



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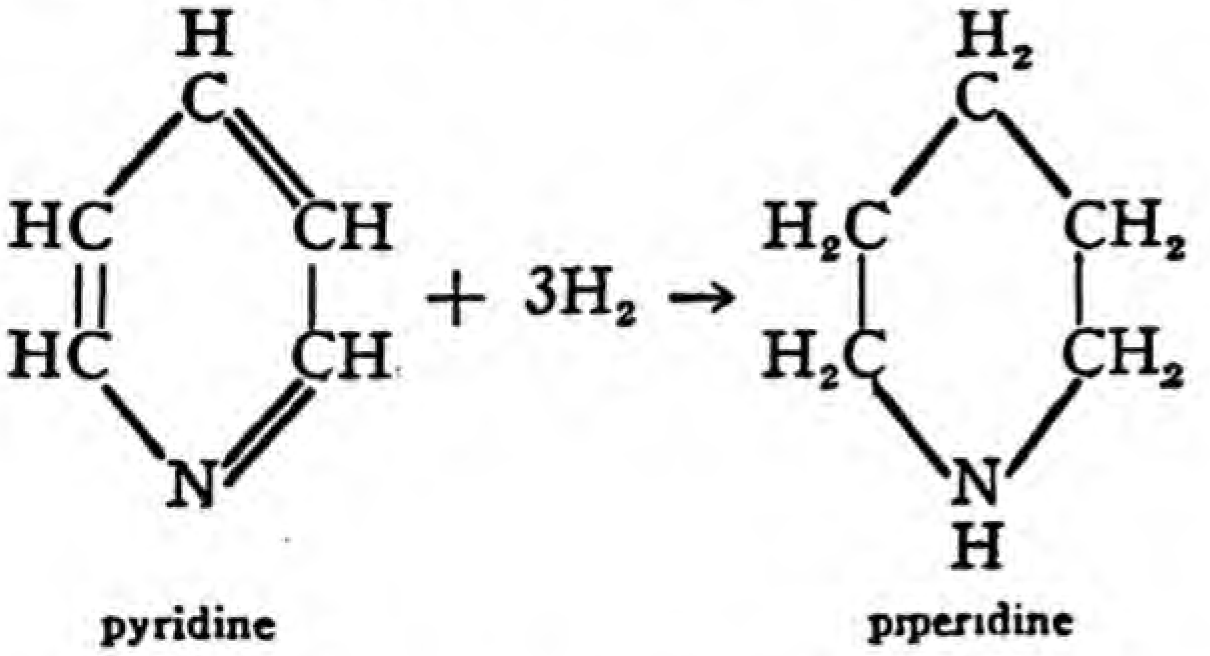
[31] Adkins, H.: *Reactions of Hydrogen with Organic Compounds over Copper Chromium Oxide and Nickel Catalysts,* Madison, The Univeristy of Wisconsin Press, 1937, p. 52.

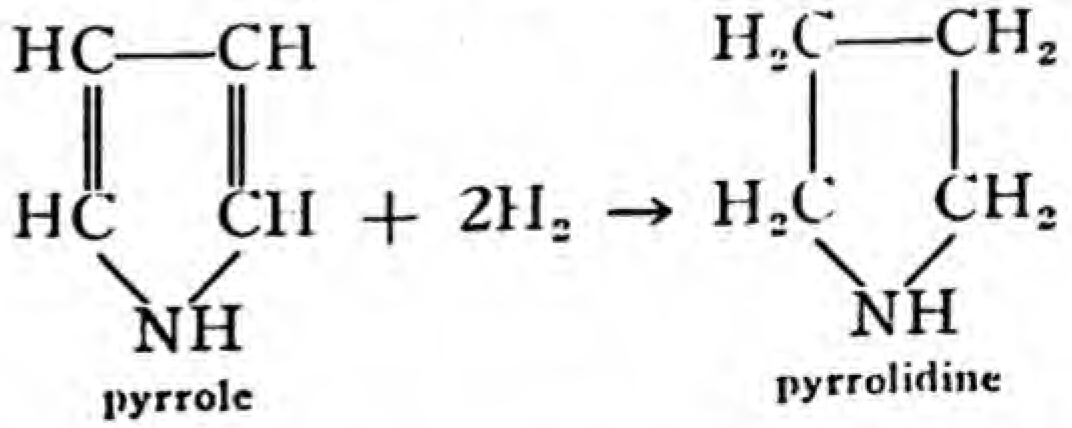
Furfural is hydrogenated to furfuryl alcohol and other alcohol derivatives at 20 to 60°C over platinum oxide.[32, 33] If copper-chromite is used at 150°C and 100 to 150 atmospheres of pressure, furfuryl alcohol is formed.[34, 35]

8. Hydrogenation of the pyridinoid nucleus:



Whereas pyridine requires higher hydrogenation temperature for conversion to piperidine than does the hydrogenation of benzene to cyclohexane, the derivatives of pyridine are generally more readily hydrogenated than the derivatives of benzene. In compounds, containing both a pyridinoid and a benzenoid ring, the former is hydrogenated first. Catalysts for this reaction are nickel on kieselguhr, Raney nickel,[34] copper-chromite,[36] and palladium on asbestos,[37] Raney nickel providing for milder hydrogenation conditions than nickel on kieselguhr.[3]

9. Hydrogenation of the pyrroloid nucleus:



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[32] Kaufmann and Adams: *J. Am. Chem. Soc.*, **45**, 3029 (1923).

[33] Pierce and Parks: *J. Am. Chem. Soc.*, **51**, 3385 (1929).

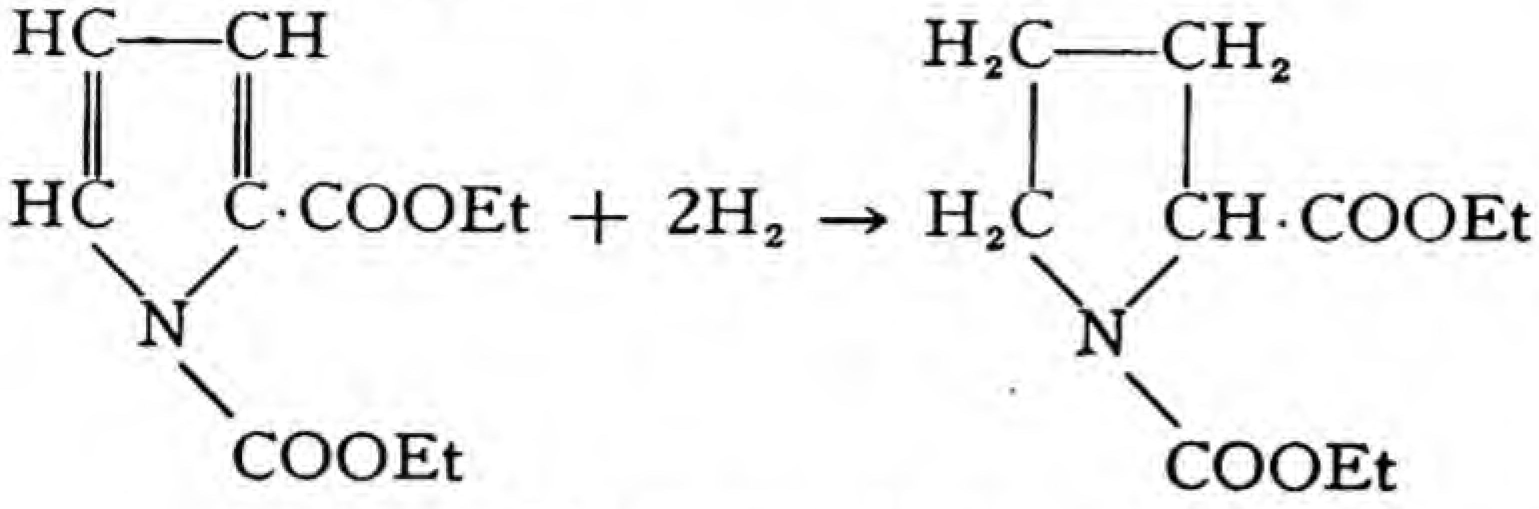
[34] Adkins and Connor: *J. Am. Chem. Soc.*, **53**, 1091 (1931); U. S. Patent 2,094,975 (1937).

[35] Adkins, Kuick, Farlow and Wojcik: *Ibid.*, **56**, 2425 (1934).

[36] Adkins and Signaigo: *Ibid.*, **58**, 709 (1936).

[37] Zelinsky and Boriskoff: *Ber.*, **57**, 150 (1924).

Hydrogenation of pyrrole, over nickel at 200°C, is slow and the yield is poor (around fifty per cent). However, if the hydrogen, attached to the nitrogen in the pyrrole ring, is substituted, the pyrroloid nucleus is hydrogenated at comparatively low temperature, i.e., 70°C or less:[36]



Hydrogenolysis

This is the process in which hydrogen reacts with an organic compound to cleave the molecule.[3, 38]

1. Carbon to metal bonds:

$$R_2Me + H_2 \xrightarrow[160\text{–}200^\circ C]{Ni} 2RH + Me$$

$$(C_6H_5)_4Pb \xrightarrow[200^\circ C]{Ni} 2C_6H_5 \cdot C_6H_5 + Pb$$

Dibutylzinc and diphenylmagnesium are split by hydrogen over nickel in the same way.[1, 39]

2. Oxygen to carbon bonds in alcohols:

$$ROH + H_2 \rightarrow RH + H_2O$$

This reaction, i.e., the reduction of primary and secondary alcohols and phenol over nickel or copper-chromite, does not proceed at temperatures below 250°C except when R contains one of the following groups: Phenyl, furyl, pyrryl, hydroxyl, carbonyl, or carbalkoxyl:[1, 40]

$$\underset{\text{benzylalcohol}}{C_6H_5 \cdot CH_2OH} + H_2 \xrightarrow[100\text{–}125^\circ C]{Ni} \underset{\text{toluene}}{C_6H_5 \cdot CH_3} + H_2O$$

---

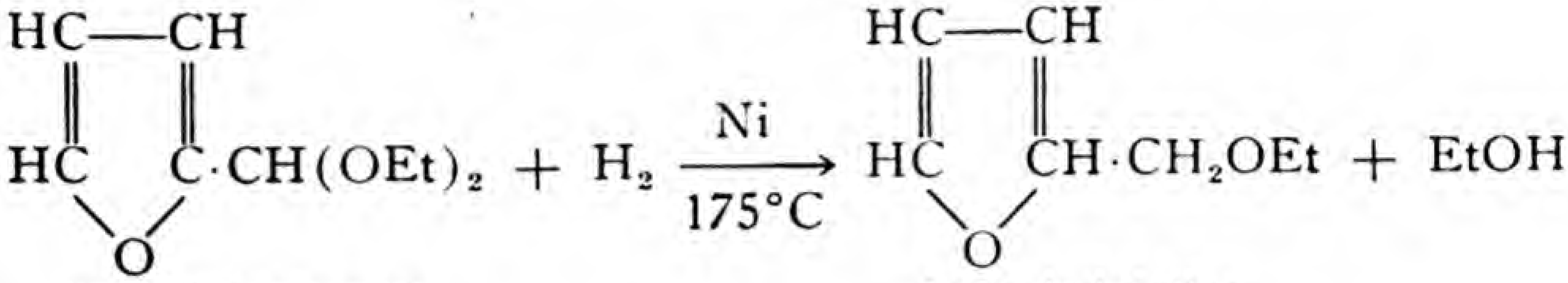
[38] Schmidt: *Z. Elektrochem.*, **39**, 824 (1933).
[39] Adkins and Zartman: *J. Am. Chem. Soc.*, **54**, 3398 (1932).
[40] Adkins, Covert and Connor: *Ibid.*, **54**, 1651 (1932).

3. Ethers:[41]

$$\mathrm{ROR'} + \mathrm{H_2} \xrightarrow[100\text{–}200^\circ\mathrm{C}]{\mathrm{Ni\ (Raney)}} \mathrm{RH} + \mathrm{R'OH}$$

4. Acetals:[1, 20]

$$\mathrm{RCH(OR')_2} + \mathrm{H_2} \xrightarrow[175^\circ\mathrm{C}]{\mathrm{Ni}} \mathrm{RCH_2OR'} + \mathrm{R'OH}$$



diethyl furfural acetal

furfural ethyl ether

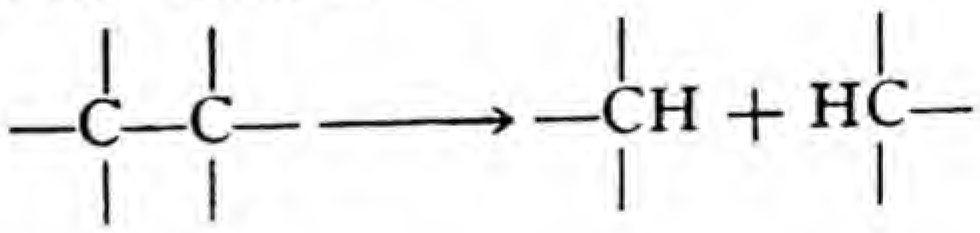
Both Raney nickel and supported nickel are used.

5. Esters and lactones:[3]

$$\mathrm{R{\cdot}COOR'} \xrightarrow[175^\circ\mathrm{C\ or\ more}]{\mathrm{Ni}} \mathrm{R{\cdot}COOH} + \mathrm{R'H}$$

This reaction is not complete unless an amine is used as a solvent to neutralize the acid produced.

6. Carbon to carbon bonds:[41a]



$$-\overset{|}{\underset{|}{\mathrm{C}}}-\overset{|}{\underset{|}{\mathrm{C}}}- \longrightarrow -\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H} + \mathrm{H}\overset{|}{\underset{|}{\mathrm{C}}}-$$

a. Hydrocarbons:[20]

$$\mathrm{(C_6H_5)_3C{\cdot}CH(C_6H_5)_2} + \mathrm{H_2} \xrightarrow[125^\circ\mathrm{C}]{\mathrm{Ni}} \mathrm{(C_6H_5)_3CH} + \mathrm{(C_6H_5)_2CH_2}$$

pentaphenyl ethane triphenyl methane diphenyl methane

b. Alcohols:[3]

$$\mathrm{R{\cdot}CH_2OH} + 2\mathrm{H_2} \xrightarrow[250^\circ\mathrm{C}]{\mathrm{Ni\ (Raney)}} \mathrm{RH} + \mathrm{CH_4} + \mathrm{H_2O}$$

---

[41] Adkins and Van Duze: *J. Am. Chem. Soc.*, **57**, 147 (1935).

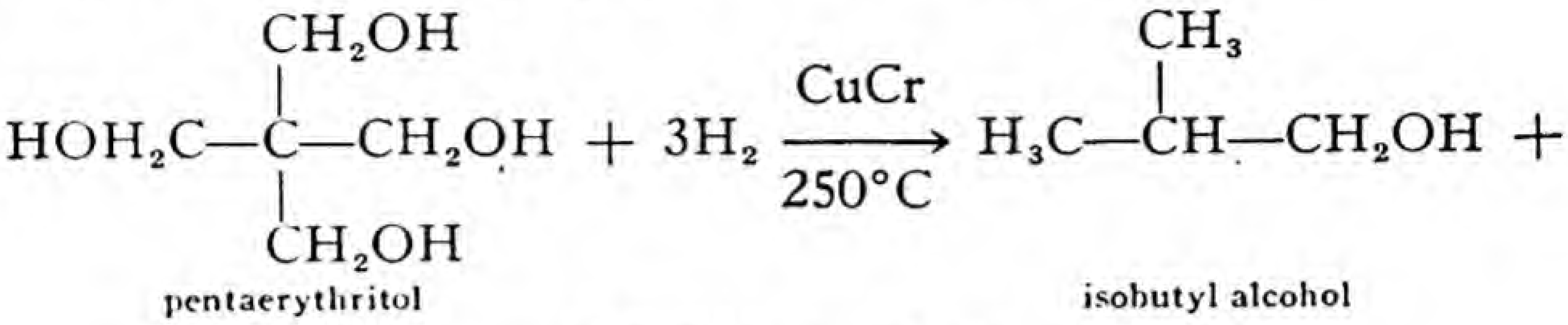
[41a] Schmidt: *Ber.*, **64**, 2051 (1931).

Adkins considers this reaction to proceed in two steps:

$$\mathrm{R{\cdot}CH_2OH + H_2 \rightarrow RH + CH_3OH}$$

$$\mathrm{CH_3OH + H_2 \rightarrow CH_4 + H_2O}$$

c. Glycols and other polyhydric alcohols:[42]

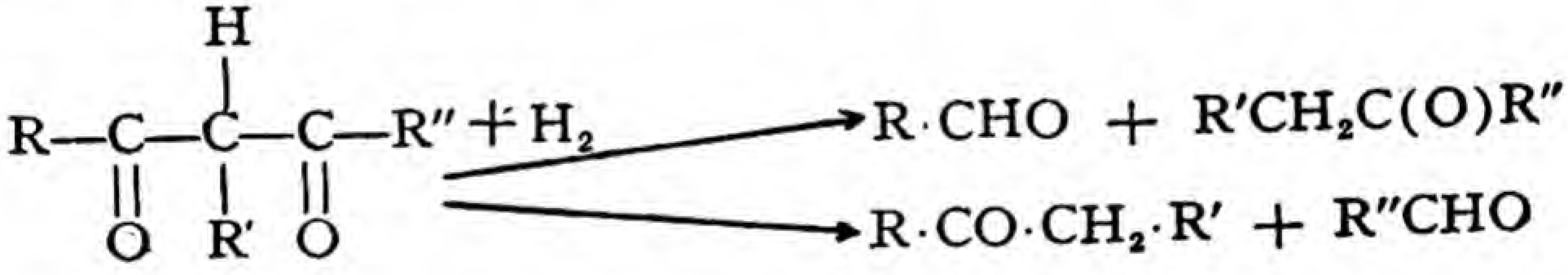


$$\underset{\text{pentaerythritol}}{\mathrm{HOH_2C{-}\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}{-}CH_2OH}} + \mathrm{3H_2} \xrightarrow[250^\circ\mathrm{C}]{\mathrm{CuCr}} \underset{\text{isobutyl alcohol}}{\mathrm{H_3C{-}\overset{\displaystyle CH_3}{CH}{-}CH_2OH}} +$$

$$\mathrm{CH_3OH + 2H_2O}$$

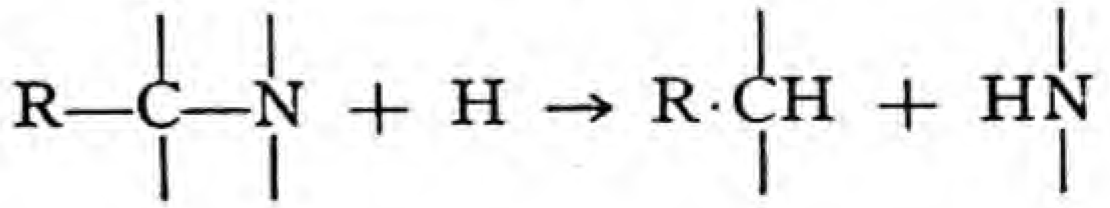
Sorbitol or mannitol hydrogenated at 250°C with copper-chromium oxide as catalyst gives a very good yield of 1,2 propylene glycol together with smaller yields of methyl alcohol and ethyl alcohol. Glucose behaves similarly.[43]

d. 1,3-diketones:[44]



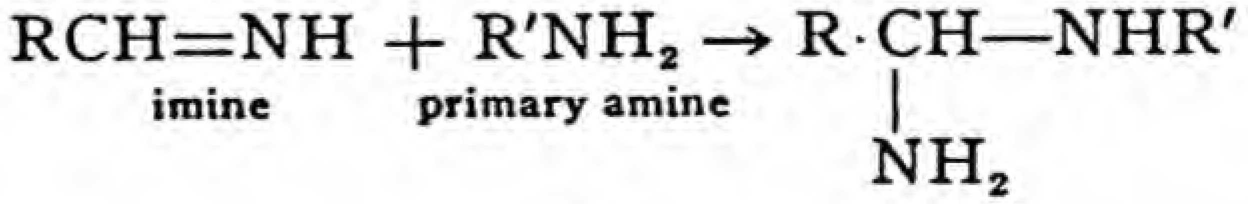
$$\mathrm{R{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}\overset{\displaystyle H}{\underset{\displaystyle R'}{C}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R'' + H_2} \begin{cases} \longrightarrow \mathrm{R{\cdot}CHO + R'CH_2C(O)R''} \\ \longrightarrow \mathrm{R{\cdot}CO{\cdot}CH_2{\cdot}R' + R''CHO} \end{cases}$$

7. Carbon to nitrogen bond:[3]

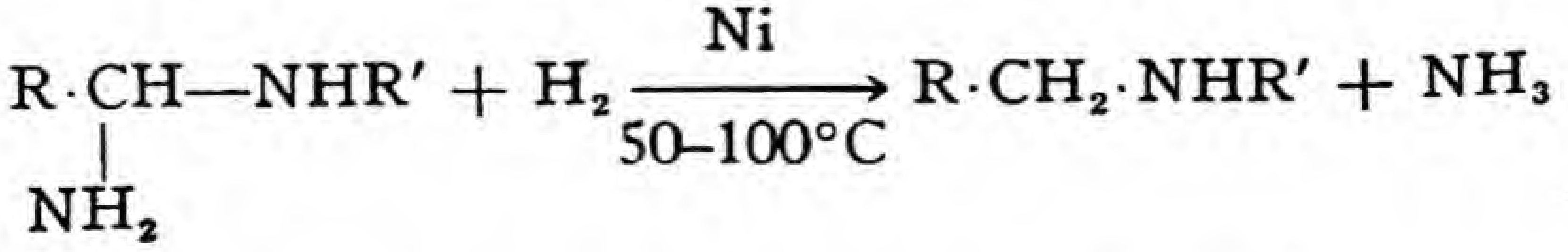


$$\mathrm{R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{N}} + H \rightarrow R{\cdot}\overset{|}{\underset{|}{C}}H + H\overset{|}{\underset{|}{N}}}$$

a. α-diamines:



$$\underset{\text{imine}}{\mathrm{RCH{=}NH}} + \underset{\text{primary amine}}{\mathrm{R'NH_2}} \rightarrow \mathrm{R{\cdot}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}NHR'}$$



$$\mathrm{R{\cdot}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}NHR' + H_2 \xrightarrow[50\text{–}100^\circ C]{Ni} R{\cdot}CH_2{\cdot}NHR' + NH_3}$$

---

[42] Adkins and Connor: *J. Am. Chem. Soc.*, **54**, 4678 (1932).

[43] Adkins and Zartman: *Ibid.*, **55**, 4559 (1933).

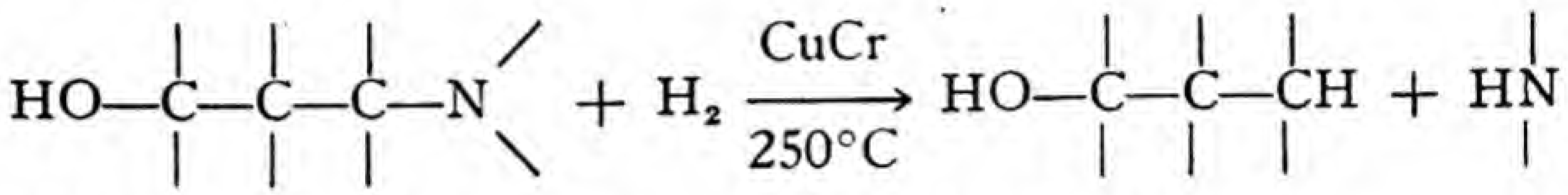
[44] Adkins and Sprague: *Ibid.*, **56**, 2669 (1934).

This method is used for preparation of secondary amines with different radicals attached to the nitrogen (Mignonac's method).

b. a-amino cyanides:

$$C_5H_{10}NH(CH_3)_2CN + 2H_2 \xrightarrow[80\text{–}100°C]{Ni\ (Raney)} \underset{\text{piperidine}}{C_5H_{10}NH} + (CH_3)_2CH\ NH_2$$

c. Amino alcohols:



$$HO{-}C{-}C{-}C{-}N\!\begin{smallmatrix}/\\ \backslash\end{smallmatrix} + H_2 \xrightarrow[250°C]{CuCr} HO{-}C{-}C{-}CH + HN$$

In this case the hydroxyl group facilitates the cleavage.

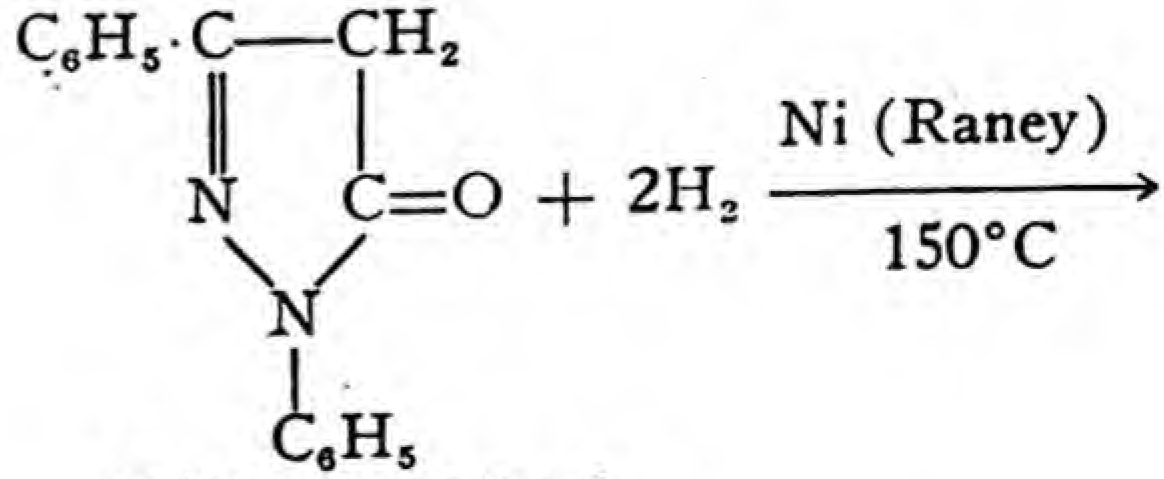
d. Hydroamides:[45]

$$RCH{=}N{-}CH(R){-}N{=}CHR + 3H_2 \xrightarrow[110\text{–}200°C]{Ni\ (Raney,\ kieselguhr)} RCH_2NH_2 + (RCH_2)_2NH$$

This nitrogen-carbon linkage is very susceptible to hydrogenolysis.

When R is a phenyl group, the yields of benzyl- and dibenzylamine were 94 to 96 per cent respectively, the reaction being completed within a few hours.

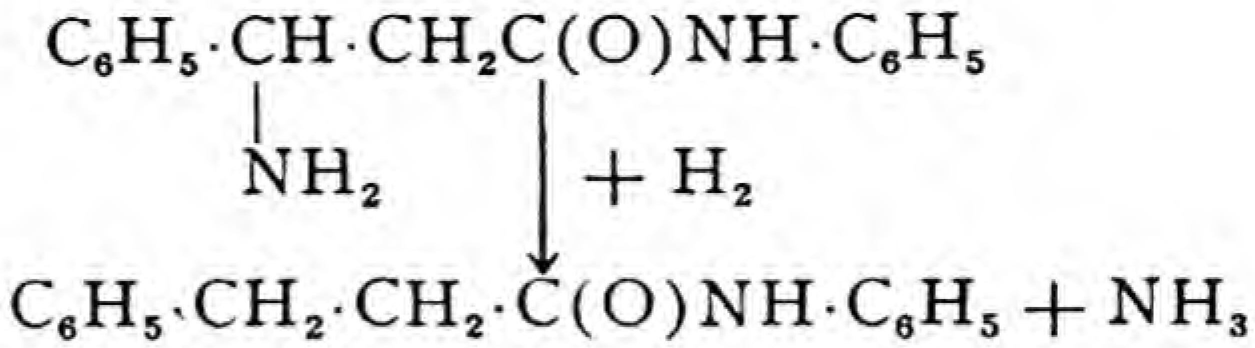
e. β-amino amides:[44a, 45]



1,3 diphenylpyrazolone-5

[44a] Adkins and Farlow: *J. Am. Chem. Soc.,* **59, 135 (1937).**

[45] Adkins and Winans: *J. Am. Chem. Soc.,* **55, 2051, 1933.**



$$\underset{\displaystyle NH_2}{C_6H_5\cdot CH}\cdot CH_2C(O)NH\cdot C_6H_5 \xrightarrow{+H_2} C_6H_5\cdot CH_2\cdot CH_2\cdot C(O)NH\cdot C_6H_5 + NH_3$$

8. Nitrogen to oxygen bond (Reductions:)

a. Oximes:[46]

$$R_2C{=}NOH + 2H_2 \xrightarrow[\text{below } 80°C]{\text{Ni (Raney)}} R_2CHNH_2 + H_2O$$

This reaction proceeds under very mild hydrogenation conditions, in fact, it starts at room temperature and proceeds by the heat evolved exothermally. It is suggested that this reaction may be used for the Knorr synthesis of pyrroles.[3]

b. Nitroso compounds:[3]

$$R\cdot NO + 2H_2 \xrightarrow[25\text{–}100°C]{\text{Ni (Raney, kieselguhr)}} R\cdot NH_2 + H_2O$$

c. Nitro compounds:

$$R\cdot NO_2 + 3H_2 \xrightarrow[100\text{–}175°C]{\text{Ni (kieselguhr) ; CuCr}} RNH_2 + 2H_2O$$

$$\underset{\text{nitrobenzene}}{C_6H_5\cdot NO_2} + 3H_2 \longrightarrow \underset{\text{aniline}}{C_6H_5\cdot NH_2} + 2H_2O$$

The conversion is almost quantitative. Raney nickel is very active and may lead to formation of azo and azoxy compounds, but it can be used quite successfully for reduction of nitro compounds in alcohol at 25 to 100°C. Raney nickel has also been used for hydrogenation of nitro aryl arsonic acids to amino arsonic acids.[47]

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[46] Adkins and Winans: *J. Am. Chem. Soc.*, **55**, 4167 (1933).

[47] Stevinson and Hamilton: *J. Am. Chem. Soc.*, **57**, 2051 (1933).

9. Nitrogen to nitrogen bond:[45]

$$R_2N{-}NR_2 + H_2 \xrightarrow[80\text{–}150°C]{Ni} 2R_2NH$$

$$\underset{\text{azo benzene}}{C_6H_5{\cdot}N{=}N{\cdot}C_6H_5} + H_2 \rightarrow \underset{\text{aniline}}{2C_6H_5{\cdot}NH_2}$$

diazoaminobenzene → aniline

1-Phenyl-3-methylpyrazolone-5 (in EtOH) → butyranilide

Benzaldazine → Benzylamine and dibenzylamine

10. Hydrogenation and hydrogenolysis of esters; preparation of alcohols and glycols from esters:[48, 49, 50]

$$R{\cdot}COOR' + 2H_2 \xrightarrow[200\text{–}250°C]{CuCr} R{\cdot}CH_2OH + R'OH$$

Some typical examples are the following:[3]

Ethyl valerate ⟶ Pentanol-1
Ethyl myristate ⟶ Tetradecanol-1
Ethyl lactate ⟶ Propanediol-1,2
Castor oil ⟶ Octadecanediol-1,12; octadecanol-1
Diethylglutarate ⟶ Pentenediol-1,5

11. Hydrogenation and hydrogenolysis of amides to amines:[3]

$$RC(O)NR'_2 + 2H_2 \xrightarrow[\substack{250\text{–}265°C \\ 200\text{–}300\ \text{atm.}}]{CuCr} RCH_2NR'_2 + H_2O$$

This reaction proceeds only under severe conditions, the general conditions for reaction being 200–300 atmospheres at 250 to 265°C in the presence of copper-chromium oxide amounting to 15 per cent of the amide, and using about 400 cc of dioxan per mol of monoamide.

Considerable work has been carried out in order to correlate the structural characteristics and the specific action of catalysts on

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[48] **Adkins, Connor and Folkers:** ***Ibid.*, 53, 1091, 1095 (1931).**

[49] **Schrauth, Schenck, and Stickhorn:** ***Ber.*, 64, 1314 (1931).**

[50] **Normann:** ***Z. angew. Chem.*, 44, 714 (1931).**

chemical compounds (see page 99). Having now discussed the action of two hydrogenation catalysts on a wide variety of compounds of different chemical characteristics, presentation of some data of hydrogenation of a single compound, with various catalysts of different crystal structure and composition, offers much interest. Such data have been supplied by Emmett and Skau[50a] who hydrogenated benzene over various catalysts. The authors review the work of the same nature by Balandin,[51] Kistiakowsky,[52] Taylor,[53] and Long, Frazer and Ott.[54] Detailed description of the preparation of the catalysts used is given. The data obtained by measuring the activity of the catalysts investigated were as follows:

Catalyst	Reduction temperature °C	Surface sq m/g	Space velocity during tests	Temperature, °C required for producing cyclohexane			Structure
				10%	50%	100%	
1. Precipitated Fe-Co catalysts:							
Co	360	6.64	3290	37	43	50	f.c.c.
Fe-CoI(25.4 + 74.6Co)	360	6.73	3430	43	55	66 some	f.c.c. b.c.c.
Fe-CoII(59.9 + 40.1Co)	400	7.69	3430	74	90	93 and	f.c.c. b.c.c.
Fe-CoIII(78.4 + 21.6Co)	400	6.34	3430	190	219	— some	b.c.c. f.c.c.
Fe	400	6.99	3430	Not active			b.c.c.
2. Copper catalysts:							
CuI(0.0006%Ni)	200	0.95	66	Not active			f.c.c.
CuII(0.001%Ni)	150	0.66	117	6.5% at 190			f.c.c.
CuIII(0.0005%Ni)	150	3.83	111	Not active			f.c.c.
CuIV(0.1%Ni)	150	5.74	93	2.1% at 200			f.c.c.
CuV(1.0%Ni)	150	7.33	121	112	142	158	f.c.c.
CuV(1.0%Ni)	350	3.92	128	155	186	—	f.c.c.
CuVI(0.0006%Ni)	150	0.72	136	1% at 220			f.c.c.
CuVII(0.0006%Ni)	150	0.58	55	1.6% at 225			f.c.c.
3. Nickel catalysts:							
NiI(Nickelous nitrate precipitated by NH_4OH)	360	0.64	2600	117	131	140	f.c.c.
NiII(Nickelous nitrate precipitated by NaOH)	360	1.52	3740	113	128	134	f.c.c.
4. Ag-Pd catalysts:							
Pd	100	0.35	3020	82	101	111	f.c.c.
Ag-PdI(20Ag + 80Pd)	100	0.82	1850	110	138	—	f.c.c.
Ag-PdII(55Ag + 45Pd)	100	0.86	1850	120	—	—	f.c.c.
Ag	100	0.45	58	Not active			f.c.c.

f.c.c. = face-centered cubic lattice; b.c.c. = body-centered cubic lattice.

[50a] Emmett and Skau: *J. Am. Chem. Soc.*, **65**, 1029 (1943).

[51] Balandin: *Z. physik. Chem.*, **B2**, 289 (1929).

[52] Kistiakowsky: *J. Am. Chem. Soc.*, **58**, 137, 146 (1936).

[53] Taylor: *J. Am. Chem. Soc.*, **60**, 627 (1938).

[54] Long, Fraser, and Ott: *Ibid.*, **56**, 1101 (1934).

Whereas these experiments confirm Balandin's conclusions as to the necessity that the substance to be hydrogenated and the surface structure of the catalyst have compatible configurations, other factors seem to be of influence too.

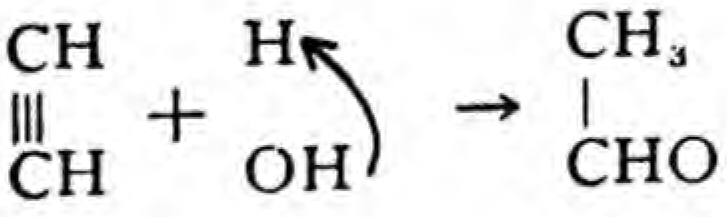
Attention should also be called to the studies on the stereochemistry of catalytic hydrogenation by Linstead et al.[5] who studied these problems on derivatives of diphenic acid and of phenanthrene hydrogenated over a platinum catalyst. This work throws considerable light on the steric problems encountered in catalysis and it is recommended for detailed study to any student of catalytic hydrogenation of aromatic compounds.

As to the kinetics of the hydrogenation reaction, reference is made to the works by Schmidt,[38] Anderson and Rowe,[55] and Beckmann, Pufahl, and Hougen.[56]

5. Hydration

This process involves the formation of a new compound by the addition of water. Catalysts are useful or required in certain cases, but hydration processes are, by no means, all catalytic.

Acetylene gas, when passed into a solution of mercuric sulfate or oxide in dilute sulfuric acid, yields acetaldehyde:[1, 2, 3, 4]



$$\begin{matrix} \mathrm{CH} \\ ||| \\ \mathrm{CH} \end{matrix} + \begin{matrix} \mathrm{H} \\ \mathrm{OH} \end{matrix} \rightarrow \begin{matrix} \mathrm{CH_3} \\ | \\ \mathrm{CHO} \end{matrix}$$

Propylene and butylene are hydrated to propyl alcohol and butyl alcohol, respectively, with bismuth, silver, or copper salts as catalysts.[5, 6] Ethyl alcohol is formed in almost 100 per cent yield by passing methyl chloride, mixed with 10 parts of water vapor, over activated charcoal impregnated with 5 per cent $ZnSO_4$ (or $CuSO_4$, $CdSO_4$ or $ZnCl_2$) at 250°C.[7, 8, 9, 10]

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[55] Anderson and Rowe: *Ind. Eng. Chem.*, **35**, 554 (1943).

[56] Beckmann, Pufahl, and Hougen: *Ind. Eng. Chem.* **35**, 554 (1943).

[1] Gluud and Schneider: *Ber.*, **57**, 254 (1924).

[2] Evans and Albertsen: *J. Am. Chem. Soc.*, **39**, 456 (1917).

[3] Vogt and Nieuwland: *Ibid.*, **39**, 456 (1917).

[4] Adams, Roman, and Sperry: *Ibid.*, **44**, 1781, 2968 (1922).

[5] Davis: British Patent 249,834 (1927).

[6] I. G. Farbenindustrie A.-G.: British Patent 324,897 (1930).

Dicyan is hydrated to oxamide in the presence of acetaldehyde:

$$(CN)_2 + 2H_2O \rightarrow (CONH_2)_2$$

It was found that the acetaldehyde reacts with dicyan in its enolform, i.e., as vinyl alcohol, $CH_2{=}CHOH$.[9] This is supported by the fact that the aldehydes which cannot form an enol modification do not act as hydration catalysts for dicyan (formaldehyde, benzaldehyde, chloralhydrate, glucose). Propionaldehyde, on the other hand, is active.

Hydration of olefins[10, 11, 12, 13] to alcohols is a reaction of immense practical importance, and a considerable number of such processes have been patented. Evell[11] has calculated the equilibria for this process at 150°C, the lowest temperature at which effective catalysts have been found for this reaction.[12] The reaction scheme for this process is when ethylene, at any pressure, P, is saturated with water vapor:

	C_2H_4	+	H_2O	$\rightleftarrows$	C_2H_5OH
At start	$P - pH_2O$		pH_2O		0
At equilibrium	$P - pH_2O - x$		$pH_2O - x$		x

Total relative mols at equilibrium $= P - x$

The equilibrium is calculated from

$$\frac{\dfrac{x}{p-x}}{\left(\dfrac{P - pH_2O - x}{p-x}\right)\left(\dfrac{pH_2O - x}{p-x}\right)} = K_N$$

p = partial pressure

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[7] Badische, Anilin-und Sodafabrik, German Patent 413,447; *Chem. Zentr.*, **96** (II), 429 (1925).

[8] Langenbeck: *Liebigs Ann. Chem.*, **469**, 16 (1929).

[9] Langenbeck, W.: *Die organischen Katalysatoren und ihre Beziehungen zu den Fermenten*, Berlin, Julius Springer, 1935.

[10] Dieckmann: *Ber.*, **49**, 2206 (1916).

[11] Evell: *Ind. Eng. Chem.*, **32**, 152 (1940).

[12] Bliss and Dodge: *Ibid.*, **29**, 19 (1937).

[13] Carpmael: British Patent 324,897 (1930).

For Keq. = $5.89 \cdot 10^{-2}$ at 150°C, the actual data are:

Pressure Atm.	K_N	Composition of incoming gases		Composition of equlibrium gases			Mol per cent C_2H_5OH in liquid condensed at 20°C	Per cent conversion in one pass (based on C_2H_4)
		pC_2H_4	pH_2O	pC_2H_4	pH_2O	pC_2H_5OH		
5	0.294	0.3	4.7	0.238	4.696	0.066	1.4	21.7
10	0.607	5.3	4.7	4.75	4.08	1.17	22.3	19.8
25	1.581	20.3	4.7	19.74	2.34	2.92	55.5	12.9
50	3.425	45.3	4.7	44.9	1.25	3.81	75.3	7.8
100	7.85	95.3	4.7	95.1	0.57	4.33	88.4	4.4
200	21.40	195.3	4.7	195.2	0.23	4.58	95.2	2.3

These are only a few examples of the many published results, but they serve to illustrate the principles of this important process.

GENERAL REFERENCES

Brown, U. S. Patents 1,873,536 (1932) and 1,907,317 (1933); Shiffler, Holm and Brooke: *Ind. Eng. Chem.*, 31, 1099, (1939); Sherlock and Swann: *Ind. Eng. Chem.*, **22**, 1048 (1930); Swann, Snow and Keyes: *Ind. Eng. Chem.*, **22**, 1048 (1930).

6. Hydrolysis

Hydrolysis is best defined chemically as a double decomposition, in which water is one of the reacting compounds.

A classic example of catalytic hydrolysis is the inversion of sucrose (cane sugar) with acids as catalyst:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{d-glucose}}{C_6H_{12}O_6} + \underset{\text{d-fructose}}{C_6H_{12}O_6}$$

Similarly, maltose (malt sugar) yields two molecules of d-glucose, and lactose (milk sugar) yields d-glucose and d-galactose.

The process is bimolecular, the true velocity constant being

$$k_{II} = \frac{1}{(a-b)} \ln \frac{a(b-x)}{b(a-x)}$$

where a and b are the concentrations of sucrose and water respectively, and x is the amount of sugar converted at time t. The concentration of water being nearly constant, the rate of conversion appears monomolecular:

$$k_1 = \frac{1}{t} \ln \frac{a}{a - x}$$

Starch and cellulose are hydrolyzed to dextrins and glucose by hydrolysis with dilute mineral acids, although the acid is not used up during the process: [1a]

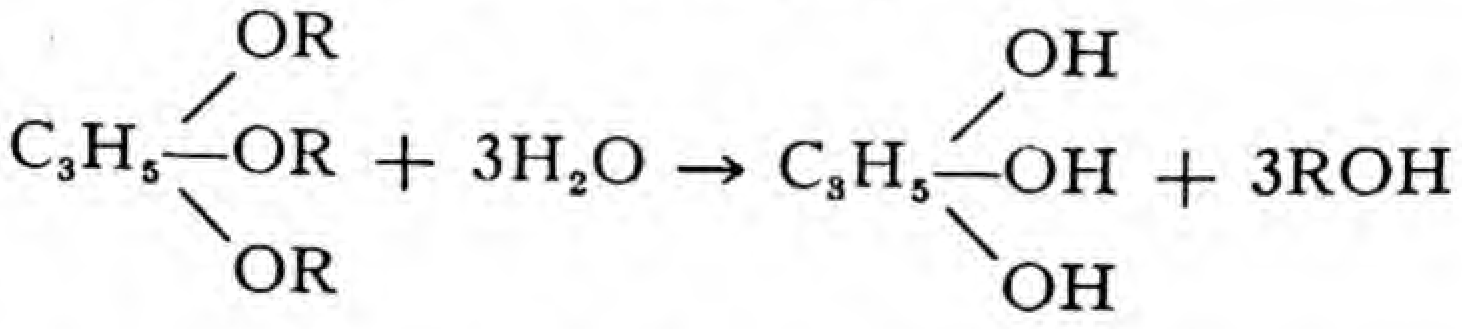
$$(C_6H_{10}O_5)_n + nH_2O \rightarrow \underset{\text{glucose}}{nC_6H_{12}O_6}$$

It should be noted that the sugar conversions are not reversible.

Hydrolysis of esters, with acids and bases as catalysts, has been studied widely. This reaction is reversible:

$$CH_3COO{\cdot}C_2H_5 + H_2O \rightleftarrows CH_3COOH + C_2H_5OH$$

Triglycerides in natural oils and fats are similarly hydrolyzed in the presence of catalysts (see page 417):



$$C_3H_5\begin{cases} OR \\ OR \\ OR \end{cases} + 3H_2O \rightarrow C_3H_5\begin{cases} OH \\ OH \\ OH \end{cases} + 3ROH$$

Langenbeck et al.[1] found that benzoyl carbinol catalyzes the hydrolysis of esters by formation of more readily hydrolyzable esters by exchange, an action which is analogous to enzyme action. An example of this is the saponification of butyric acid methyl ester at pH 8.3 with benzoyl carbinol as catalyst:

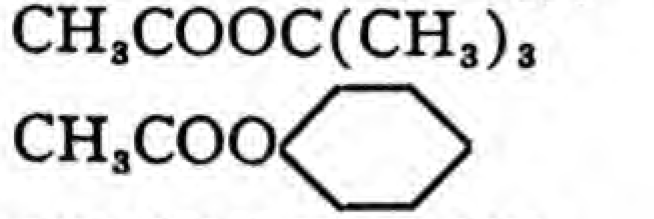
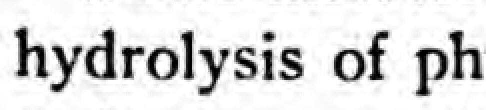
$$C_3H_7{\cdot}COOCH_3 + C_6H_5{\cdot}CO{\cdot}CHOH \rightleftarrows$$
$$C_3H_7COO{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5 + CH_3OH$$

[1a] Radley, J. A.: *Starch and Its Derivatives*, London, Chapman and Hall, Ltd., 1943.

[1] Langenbeck et al.: *Ber.*, **67B**, 384 (1934); *ibid.*, **69B**, 514 (1936); Langenbeck, W.: *Die organischen Katalysatoren und ihre Beziehungen zu den Fermenten*, Berlin, Julius Springer, 1935, p. 59.

$$C_3H_7{\cdot}COO{\cdot}CH{\cdot}CO{\cdot}C_6H_5 + H_2O \rightarrow C_3H_7COOH + C_6H_5{\cdot}CO{\cdot}CH_2OH$$

Skrabal et al.[2] have shown that the velocity of the acid hydrolysis of esters increases with increasing influence of the alcohol on the activity of the ester molecule; and that similarly, the velocity in alkaline hydrolysis increases with increasing influence of the acid. The following data illustrate this:[2]

	Velocity constants	
Ester	Acid hydrolysis	Alkaline hydrolysis
$HCOOCH_3$	0.145	2400
$(COOCH_3)_2$	0.00960	880000
$CH_2(COOCH_3)_2$	0.00103	73.5
$CH_2(OCH_3)COOC_2H_5$	0.00380	128
$CH_2(OH)COOC_2H_5$	0.00683	65.3
$CH_3CHOHCOOC_2H_5$	0.00761	63.7
$CH_2(OH)CH(OH)COOC_2H_5$	0.00185	57.3
$CH_3COCOOC_2H_5$	0.00816	110000
$CH_3COCH_2COOC_2H_5$	0.00099	28.6
$CH_3COCH_2CH_2COOC_2H_5$	0.00156	7.7
$CH_3CH_2CH_2COOC_2H_5$	0.00521	3.85
 $CH_3CHCH_2CH_2CO{\cdot}O$	0.0106	24.7
$(CH_3COO)_2CH_2$	0.00402	476
$(CH_3COO)_2CHCH_3$	0.00345	65
$(CH_3COOCH_2)_4C$	0.00432	205
$CH_3COOCH(CH_3)_2$	0.00360	1.78
$CH_3COOC(CH_3)_3$	0.00740	0.116
	0.00464	82
$CH_3COOCH{=}CH_2$	0.00813	630
$CH_3COOCH_2CH_3$	0.00658	6.46
$(CH_3)_3CCOOC_2H_5$	0.00292	1.66

Some interesting data were obtained in a study of the alkaline hydrolysis of phthalic acid esters with 0.25 N NaOH free from carbonate as catalyst:[2a]

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[2] Skrabal et al., *Z. Elektrochem.*, 33, 340 (1927).

[2a] Kivinen and Tommila: *Suomen Kemistilehti*, **14B**, 7 (1941); *Chem. Abstracts*, **36**, 21 (1942).

	Rate Constant, k, at different temperatures, °C:				Activation energy, cals.
Acid	0°	15°	25°	40°	
1. Terephthalic acid diethyl ester	0.00675	0.0252	0.0537	0.143	13,000
2. Isophthalic acid diethyl ester	0.00303	0.0105	0.0232	0.0702	13,300
3. Phthalic acid diethyl ester	0.000481	0.00177	0.00358	0.0102	12,870

These data were compared with data obtained by studying the alkaline hydrolysis of benzoic acid esters, and from it was concluded that the second, intact, ester group exerts strong accelerating and electron-attracting properties, its action being only slightly less than that of a nitro group. Furthermore, a plot of the activation energies of terephthalic and isophthalic acid diethyl esters and benzoyl acetate against the logarithms of the rate constant, k, gives a straight line ($\text{slope} = -2.303\ RT$), which suggests that the differences in reaction rates are due to differences in activation energy. The values of phthalic acid diethyl ester fall far below that line, and from this the conclusion was drawn that the accelerating action of the intact ester group is strongest in the ortho position.[2a]

Stieglitz[3] studied the hydrolysis of imido esters, which is catalyzed by strong acids:

$$R\cdot C(=NH)\cdot OR' + H_2O \rightarrow R\cdot CO\cdot OR' + NH_3$$

This catalysis was interpreted as being due to the formation of an intermediary ion complex of the ester with the hydrogen ion.

The hydrolysis of ethyl acetate, in an aqueous solution of equal concentration of hydrogen and hydroxyl ions, is in its early stages catalyzed predominantly by hydroxyl ions, and as the hydrolysis proceeds and the acid concentration increases, the hydrogen ion catalysis increases. Consequently, the velocity of the ester hydrolysis, in this case, increases to a maximum, decreases to a minimum, and then increases again.[4]

Much has been published about the theory of ester hydrolysis.

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[3] Stieglitz: *J. Am. Chem. Soc.*, **32**, 221 (1910); *ibid.*, **35**, 1774 (1913).

[4] Brönsted, J. N.: *Physical Chemistry*, London, William Heinemann, Ltd., 1937.

and attention is called to the works by Polányi and Szabó,[5] Newling and Hinshelwood,[6] Mumm,[7] and others.

Ethers are hydrolyzed, in the presence of dilute acids, to alcohols. This hydrolysis also has been investigated by Skrabal et al.[9] The velocity constants (K) of the acid hydrolysis of various ethers at 25°C, calculated on one ether oxygen atom, was found to be as follows:

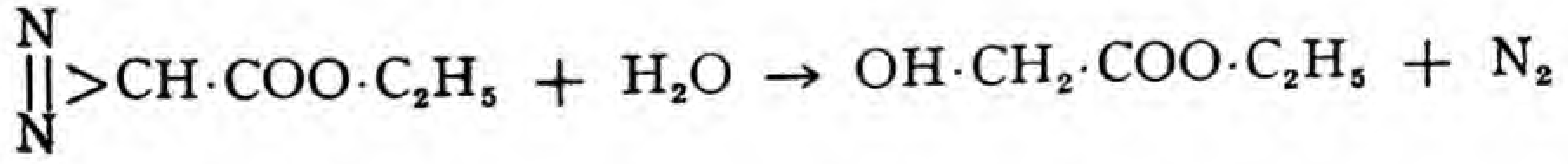
Compound	K
Ethylether	0.00000000000146
Diisopropylether	0.000000000659
Vinylether	173

The conversion of ether to alcohol in vapor-phase at 275-300°C and 120 atmospheres pressure, using as catalyst aluminum oxide with five per cent nickel, has been reported on by Balandin et al.[10]

The hydrolysis of organic halides, especially chlorinated hydrocarbons, is of increasing technical importance. The rate of the hydrolysis depends on the nature of the solvent and the structure of the hydrocarbon.[11] Aromatic halides hydrolyze with much more difficulty than do paraffinic halides. Phenol is made commercially by hydrolysis of chlorobenzene, small amounts of copper facilitating this reaction:[12]

$$C_6H_5Cl + Na_2CO_3 \cdot aq. \rightarrow C_6H_5OH + NaCl + NaHCO_3 \cdot aq.$$

Diazoacetic esters in aqueous solution are hydrolyzed according to:



$$\overset{N}{\underset{N}{\|}}{>}CH \cdot COO \cdot C_2H_5 + H_2O \rightarrow OH \cdot CH_2 \cdot COO \cdot C_2H_5 + N_2$$

---

[5] Polányi and Szabó: *Trans. Faraday Soc.*, **30**, 508 (1934).

[6] Newling and Hinshelwood: *J. Chem. Soc.*, 1357 (1936).

[7] Mumm: *Ber.*, **72B**, 1874 (1939).

[9] Skrabal et al.: *Z. physik. Chem.*, **A169**, 177 (1934).

[10] Balandin et al.: *Ber.*, **65B**, 1557 (1932).

[11] Hughes et al.: *J. Chem. Soc.*, 1177, 1183, 1187 (1937); *J. Am. Chem. Soc.*, **57**, 708 (1935).

[12] Lloyd, S. J., and G. D. Palmer: Hydrolysis, Chapter XI in Groggins' *Unit Processes in Organic Synthesis*, New York, McGraw-Hill Book Company, Inc., 1938, p. 590.

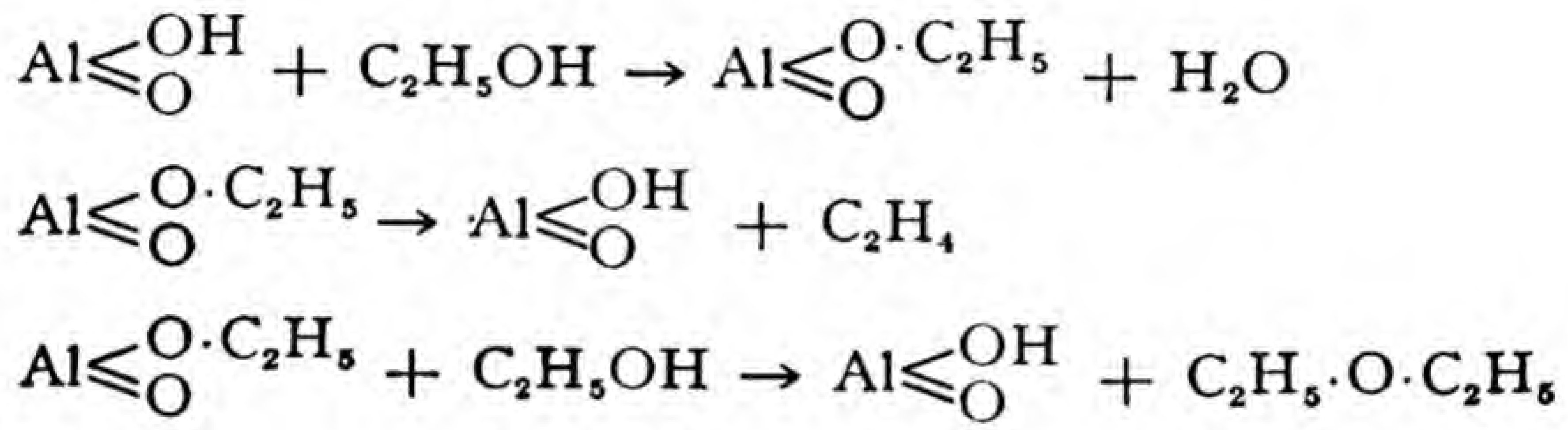
This reaction is catalyzed by acids, the rate of evolution of nitrogen being proportional to the hydrogen ion concentration.[13]

7. Dehydration

A considerable number of chemical reactions are known which consist in the elimination of water from an organic compound.[1, 2, 3]

Ipatieff [2, 3] has shown the analogy which exists between the action of sulfuric acid on alcohol and dehydration of alcohol over alumina and thoria:

(a) Alumina:

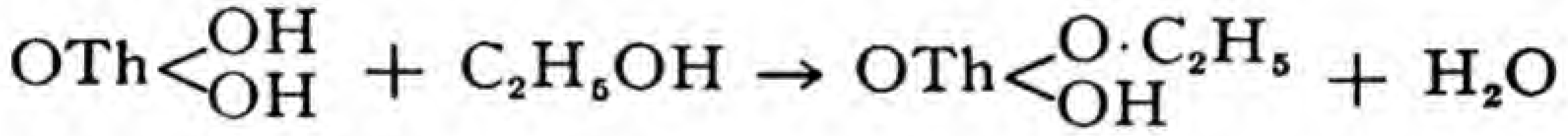


1. $\mathrm{Al}\leqslant^{\mathrm{OH}}_{\mathrm{O}} + C_2H_5OH \rightarrow \mathrm{Al}\leqslant^{\mathrm{O\cdot C_2H_5}}_{\mathrm{O}} + H_2O$

2. $\mathrm{Al}\leqslant^{\mathrm{O\cdot C_2H_5}}_{\mathrm{O}} \rightarrow \mathrm{Al}\leqslant^{\mathrm{OH}}_{\mathrm{O}} + C_2H_4$

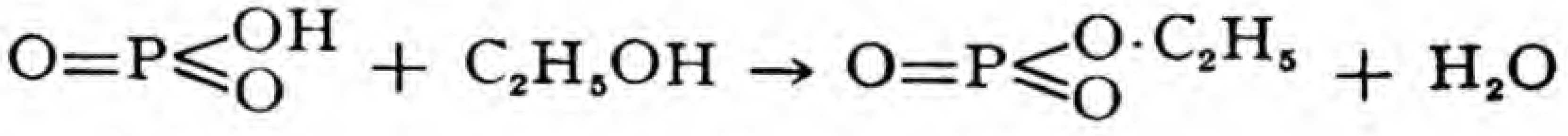
3. $\mathrm{Al}\leqslant^{\mathrm{O\cdot C_2H_5}}_{\mathrm{O}} + C_2H_5OH \rightarrow \mathrm{Al}\leqslant^{\mathrm{OH}}_{\mathrm{O}} + C_2H_5{\cdot}O{\cdot}C_2H_5$

(b) Thoria:



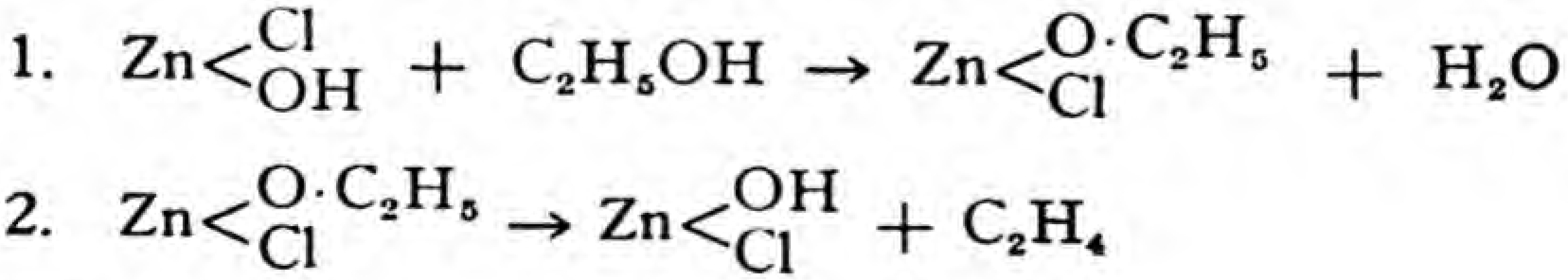
$$\mathrm{OTh}<^{\mathrm{OH}}_{\mathrm{OH}} + C_2H_5OH \rightarrow \mathrm{OTh}<^{\mathrm{O\cdot C_2H_5}}_{\mathrm{OH}} + H_2O$$

(c) Orthophosphoric acid:



$$\mathrm{O{=}P}\leqslant^{\mathrm{OH}}_{\mathrm{O}} + C_2H_5OH \rightarrow \mathrm{O{=}P}\leqslant^{\mathrm{O\cdot C_2H_5}}_{\mathrm{O}} + H_2O$$

(d) Zinc chloride: (oxychloride forms in the presence of water)



1. $\mathrm{Zn}<^{\mathrm{Cl}}_{\mathrm{OH}} + C_2H_5OH \rightarrow \mathrm{Zn}<^{\mathrm{O\cdot C_2H_5}}_{\mathrm{Cl}} + H_2O$

2. $\mathrm{Zn}<^{\mathrm{O\cdot C_2H_5}}_{\mathrm{Cl}} \rightarrow \mathrm{Zn}<^{\mathrm{OH}}_{\mathrm{Cl}} + C_2H_4$

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[13] Bredig and Frankel: *Ber.*, **60**, 202 (1907).

[1] Sabatier, P.: *La Catalyse en Chimie Organique.* Librairie Polytechnique, Paris, 1920, p. 267; P. Sabatier and E. Emmett Reid: *Catalysis in Organic Chemistry*, New York, D. Van Nostrand, 1937.

[2] Ipatieff, W. N., N. Orlow, and A. Petrow: *Aluminiumoxyd als Katalysator in der organischen Chemie*, Leipzig, Akademische Verlagsgesellschaft m.b.H., 1929.

[3] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures,* New York, The Macmillan Company, 1937, p. 552.

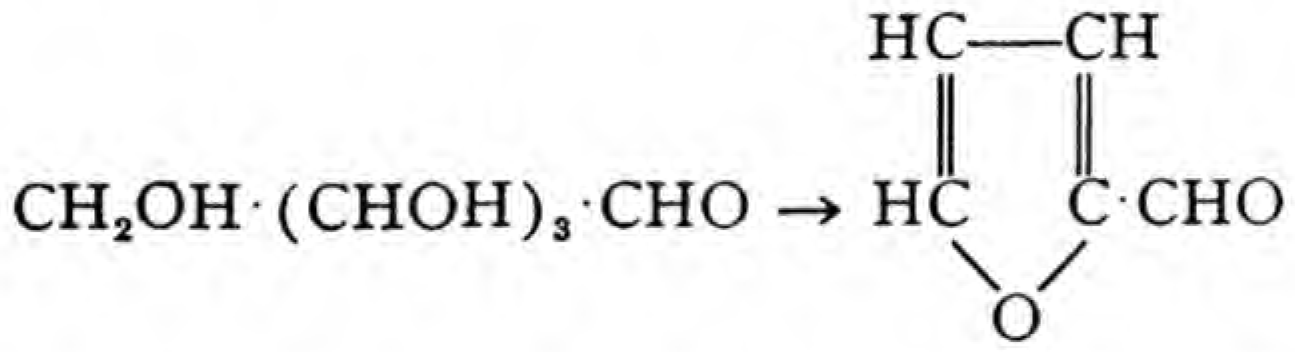
Solid phosphoric acid is an excellent catalyst for the production of dimethyl ether from methanol. This is a special case of dehydration of alcohols because an olefin cannot be formed. This catalyst catalyzes the reaction between ethyl and methyl alcohols to form ethyl methyl ether, between diethyl and dimethyl ethers to form ethyl methyl ether, and between benzyl and methyl alcohols to form benzyl methyl ether.[4]

Methyl ether is made by passing methyl alcohol at 350 to 400°C and 15 atmospheres pressure and a space velocity of about 5000 over an aluminum phosphate catalyst.[4a]

The conversion of glycerine to acrolein is facilitated by adding small amounts of alumina, aluminum sulfate, or potassium bisulfate at a temperature of about 110°C:[5]

$$CH_2OH \cdot CHOH \cdot CH_2OH \rightarrow CH_2{=}CH \cdot CHO$$

Pentoses, e.g., arabinose, are dehydrated to form a furfuran ring:[6]



Catalysis is involved in the dehydration of amides, suitable catalysts being pumice, alumina, sand, and graphite, in decreasing order:[7]

$$R \cdot CO \cdot NH_2 \rightarrow R \cdot CN + H_2O$$

Reid et al.[8] prepared cyanides from the vapors of organic acids or esters mixed with an excess of ammonia in the presence of silica gel at 500°C:

$$CH_3COOH + NH_3 \rightarrow CH_3CN + 2H_2O$$

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[4] Ipatieff and Burwell: *J. Am. Chem. Soc.*, **63**, 969 (1941).

[4a] Woodhouse: U. S. Patents 1,949,344 (1934) and 2,014,408 (1935).

[5] Senderens: *Bull. soc. chim.*, (4), **3**, 828 (1908); *Chem. Rev.*, **151**, 530 (1910).

[6] Stone and Tollens: *Liebigs Ann. Chem.*, **249**, 237 (1889).

[7] Beckers and Andrews: *J. Am. Chem. Soc.*, **38**, 2503 (1916).

[8] Reid et al.: *J. Am. Chem. Soc.*, **38**, 2128 (1916); **53**, 321 (1931).

In this way, the following cyanides were prepared: methyl cyanide (95% yield), ethyl cyanide (85%), propyl cyanide (90%), n-butyl cyanide (80%), isobutyl cyanide (94%), n-pentyl cyanide (90%), n-hexyl cyanide (93%), n-undecyl cyanide (55%), benzyl cyanide (87%), phenyl ethyl cyanide (81%). No cyanide was obtained from palmitic acid. Thoria or alumina may also be used for this reaction, but silica gel is best.[8]

Acetic acid is dehydrated to acetic anhydride, the catalyst used being orthophosphoric acid on pumice, kieselguhr, or silicon carbide:[9]

$$2CH_3COOH \rightleftarrows (CH_3COO)_2O + H_2O$$

Acetic anhydride is dehydrated to ketene at 635°C with aluminum sulfate as catalyst:[10]

$$(CH_3COO)_2O \rightleftarrows 2CH_2{=}CO + H_2O$$

The production of ketene and diketene has been discussed in detail.[11, 12]

GENERAL REFERENCE

Brown and Reid: *J. Phys. Chem.*, **28**, 1067, 1077 (1924).

8. Esterification

A most illuminating description of esterification, in its broadest sense, has been given by Emmett Reid, who classifies esterification reactions as follows: *[1, 2]

I. Two compounds react to give an ester and a second compound:

a. Reaction of an alcohol directly with an organic or inorganic acid

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[9] Dreyfus: British Patents 280,972 (1927) and 312,733 (1929).

[10] The Ketoid Co.: British Patent 237,573 (1926).

[11] Morey: *Ind. Eng. Chem.*, **31**, 1129 (1939).

[12] Boese: *Ibid.*, **32**, 16 (1940).

* This classification is included by permission of Professor E. Emmett Reid and McGraw-Hill Book Company, Inc.

[1] Reid: *Ind. Eng. Chem.*, **29**, 1344 (1937).

[2] Reid, E. Emmett: Esterification, Chapter X of Groggins' *Unit Processes in Organic Synthesis*, New York, McGraw-Hill Book Company, Inc., 1938, p. 533.

b. Alcoholysis, i.e., displacement of an alcohol by another alcohol
c. Acidolysis, i.e., displacement of an acid by another acid
d. Exchange of alkyl groups between two esters
e. Reaction between an amide and an alcohol
f. Reaction of an acid anhydride or chloride with an alcohol, phenol, or the sodium derivatives of these compounds
g. Reaction between the salt of an acid and an alkyl or aralkyl halide

II. Ester formation by the addition of one compound to another:

a. Anhydride of a dibasic acid with an alcohol or a sodium alcoholate
b. Reaction between ketene or phenyl isocyanate and an alcohol
c. Addition of ethylene to acids
d. Acetylene and acetic acid form vinyl acetate when one molecule of acid is taken up, and ethylidene acetate when two molecules are taken up
e. Preparation of esters from nitriles

III. Miscellaneous:

a. Ethylene oxide and an acid for preparation of mono-esters of glycol
b. Ester from the combination of two molecules of an aldehyde
c. Ester from carbon monoxide and alcohol

The formation of an ester by heating an alcohol with an acid is a reversible and bimolecular change, the equilibrium point of which depends on the conditions for the reaction

$$\mathrm{ROH} + \mathrm{R'COOH} \rightleftarrows \mathrm{R'COOR} + \mathrm{H_2O}$$

By using an excess of alcohol, a higher conversion is achieved. Equivalent amounts of acetic acid and ethyl alcohol are converted to about 66 per cent into ethylacetate. The reason for the limit of conversion is that the ester is hydrolyzed by the water formed during the conversion. Higher esters and esters of the aromatic series are less readily hydrolyzed and, consequently, possess a higher degree of conversion at equilibrium. In the preparation of ethylacetate, sulfuric acid may be added in order to absorb the water formed during the reaction. This process is catalyzed by small amounts of dry hydrogen chloride and concentrated sulfuric acid.

At the point of equilibrium, the following equation expresses the law of mass action for equivalent amounts of alcohol and acid:

$$k_1(a - x)(b - x) = k_2x^2$$

The esterification reaction was studied by Berthelot and St. Gilles as far back as in 1862,[3] and since then a very considerable amount of work has been carried out on these reactions.[1, 2, 4, 5, 6]

In order to obtain a high yield, the water formed upon esterification must be separated from the ester. This may be achieved by distilling off the water by adding to the esterification mixture liquids which are insoluble in water, but which distill over with water below its boiling point. Some examples of these liquids are ethylene chloride, carbon tetrachloride, benzene, etc. Of course, the ester itself may be distilled off if it has a low boiling point, such as ethyl nitrite (b.p. 16.4°C).[2]

The number of esterification catalysts is considerable, some examples being: acids, acid salts, organic compounds, sulfonic acids, zinc chloride, neutral salts (act by combining with water), metallic soaps, base-exchange materials,[4, 5, 7] oxides,[6] phosphotungstic acid,[9] dioxanates of the chlorides of Sn, Al, Zn, and Fe,[10] acid chlorides,[11] and silica gel.[11a]

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[3] Berthelot and St. Gilles: *Ann. chim.*, (3), **65**, 385 (1862); *ibid.*, **66**, 5 (1862); *ibid.*, **66**, 5 (1862); *ibid.*, **68**, 225 (1863).

[4] Keys: *Ind. Eng. Chem.*, **24**, 1344 (1937).

[5] Menschutkin: *Z. phys. Chem.*, **1**, 611 (1887); *ibid.*, **9**, 237 (1892); *Ber.*, **42**, 4020 (1909).

[6] Reid et al.: *J. Am. Chem. Soc.*, **37**, 1934 (1915); *ibid.*, **38**, 2746, 2757 (1916); *ibid.*, **39**, 1930 (1917).

[7] Sabatier, P. and E. Emmett Reid: *Catalysis in Organic Chemistry*, New York, D. Van Nostrand Company, p. 746.

[9] Lazier: U. S. Patent 2,174,985 (1939).

[10] Lazier: U. S. Patent 2,257,384 (1942).

[11] Freudenberg and Jacob: *Ber.*, **74B**, 1001 (1941); *Chem. Abstracts*, **35**, 7371 (1941).

[11a] Milligan, Chappel and Reid: *J. Phys. Chem.*, **28**, 872 (1924).

Esterification may also be accomplished in vapor phase reactions, using various oxides as catalysts. In a recent experiment on the esterification rate of acetic acid with ethyl alcohol in vapor phase, using silica gel as catalyst, it was found that the rate of vapor-phase esterification is controlled by the rate of mass transfer or diffusion through a condensed phase present in the capillaries of the silica gel. It was also noted that the second-order reaction, commonly occurring in esterification reactions in the liquid phase, was negligible in the vapor-phase reaction.[15]

Another type of esterification is that of the mercaptans:[6]

$$R{\cdot}COOH + HSR' \rightleftarrows R{\cdot}CO{\cdot}S{\cdot}R' + H_2O$$

The yields are not very high.

In alcoholysis the alcohol in an ester is displaced by another alcohol:

$$R{\cdot}COO{\cdot}R' + R''OH \rightleftarrows R{\cdot}COO{\cdot}R'' + R'OH$$

The alcoholysis reaction is very fast. It is catalyzed by strong acids, sodium, sodium alcoholate, ammonia, pyridine, and aromatic sulfonic acids.[20, 21, 22, 23] Alcohols of low molecular weight can be replaced by alcohols of high molecular weight or phenols. This principle has been used in studies on lignin,[17] in pulping wood by means of butyl alcohol,[16, 17, 18] and in exchange esterification of vegetable oils.[19]

Acidolysis is a reaction between an ester and an acid where the acid in the ester is replaced:

$$R{\cdot}COOR' + R''COOH \rightleftarrows R''COOR' + R{\cdot}COOH$$

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[15] Hoerig, Hanson, and Kowalke: *Ind. Eng. Chem.*, **35**, 575 (1943).

[16] Bailey: *Ind. Eng. Chem.*, **34**, 483 (1942).

[17] Hibbert et al.: *J. Am. Chem. Soc.*, **63**, 3035, 3041 (1941).

[18] Charbonnier: *Paper Trade J.*, **114**, 31 (1942).

[19] Blagonravova and Antipova: *Byull. Obmena Opyt. Lakokrasoch. Prom.*, No. 10, 18–19 (1940); *Chem. Abstracts*, **35**, 5731 (1941).

[20] Millar: *Z. phys. Chem.*, **85**, 129 (1913).

[21] Gibby and Waters: *J. Chem. Soc.*, 2643 (1932).

[22] Friedel and Crafts: *Liebigs Ann. Chem.*, **130**, 198 (1864); *ibid.*, **133**, 207 (1865).

[23] Adkins and Fehlandt: *J. Am. Chem. Soc.*, **57**, 193 (1935).

Carbon monoxide is added to an ether or an alcohol. With an ether the reaction is:[24, 25] $(C_nH_{2n+1})_2O + CO \rightarrow C_nH_{2n+1}COOC_nH_{2n+1}$; and with an alcohol: $2CH_3OH + CO \rightarrow CH_3COOCH_3 + H_2O$.

With an alcohol, the acid is formed intermediately and then esterified by the excess of alcohol. High pressures are an advantage, and pressures up to 700 atmospheres are used. At the time when this publication appeared, temperatures from 20 to 400°C were reported. Generally speaking, activated charcoal, metal oxides, and acidic salts are favored catalysts although sodium alcoholate may also be used.[1]

Ketene,[26] $CH_2{=}CO$, is used in the preparation of organic esters. Butylacetate is formed with butyl alcohol; as the alcohol becomes diluted, the ketene reacts less and less readily until a concentration of 75 per cent butylacetate is reached, when no further reaction takes place, if no catalyst is present. This reaction is catalyzed by sulfuric acid, water, and sodium acetate. Even tertiary butyl alcohol is easily esterified with ketene when sulfuric acid is used as catalyst.

Primary alcohols are esterified in the absence of acids at 220–310°C in the presence of a catalyst consisting of CuO and 10 per cent UO_3 according to the general scheme:[27]

$$2R\cdot CH_2OH \rightarrow R\cdot COOCH_2R + 2H_2$$

In the case of two different alcohols, the reaction is as follows:

$$4R\cdot CH_2OH + 4R'\cdot CH_2OH \rightarrow R\cdot COOCH_2R + R'COOR' + RCOOCH_2R' + R'\cdot COOCH_2R + 8H_2$$

The development of side reactions is negligible in all cases.

Starch esters, prepared from various starches and acetic anhydride or acid chlorides, have been studied very extensively.[28, 29]

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[24] Woodhouse: U. S. Patents 1,979,518, 1,979,519 (1934), and 2,019,754 (1935).

[25] Dreyfus: U. S. Patents 1,879,605 and 1,879,606 (1932).

[26] Morey: *Ind. Eng. Chem.*, **31**, 1129 (1939).

[27] Ivannikov: *J. Applied Chem. (U.S.S.R.)*, **13**, 118 (1940); *Chem. Abstracts*, **34**, 7847 (1940).

[28] Mullen and Mascu: *Ind. Eng. Chem.*, **34**, 1209 (1942).

[29] Mack and Shreve: *Ibid.*, **34**, 304 (1942).

Many catalysts have been used: Sulfuric acid, hydrochloric acid gas, zinc chloride, Twitchell acids, pyridine, potassium thiocyanate, quinoline, etc.

Various catalysts are also used in the manufacture of cellulose acetate: Inorganic acids and their derivatives, organic acids, salts, bases, halogens, etc.[30]

GENERAL REFERENCES

Sabatier and Mailhe: *Compt. rend.*, **150**, 823 (1910); Knox and Burbidge: *J. Am. Chem. Soc.*, **65**, 999 (1943); Vernon and Brown: *Ind. Eng. Chem.*, **33**, 1289 (1941); Rohm & Haas A.-G.: British Patent 520,164 (1940).

9. Halogenation

The process of introducing halogens into an organic compound is of increasing industrial interest. For economic reasons, chlorine is the most important halogen in technical halogenations, although for certain derivatives bromine may be preferred, and of late, fluorine is becoming an increasingly important halogenation agent.

The first halogen atom combines most readily with an organic compound, the subsequent halogen atoms combining with more difficulty. Chlorine and bromine are, in many cases, introduced directly into organic compounds, and it is a well known fact that mixtures of hydrocarbon gases with these two halogens readily explode.

When halogen replaces hydrogen in the benzene nucleus, the resulting products are very stable; however, if the replacement of hydrogen with halogen takes place in a side chain, the compounds formed are very reactive and resemble paraffinic derivatives. In the cold, in darkness, or when iodine is added, substitution takes place in the side chain.

A peculiar and very useful mechanism is that of halogen carriers (catalysts), which act by splitting the halogen into atoms which, in their nascent state, are very reactive. Thus, iodine trichloride acts as a carrier as follows:

$$ICl_3 \rightarrow ICl + 2Cl$$

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[30] Krüger, D.: *Zelluloseacetate und die anderen organischen Ester der Cellulose.* Berlin, Verlag von Theo. Steinkopff, 1937.

From two to twelve per cent of iodine, on the basis of the chloride content, serves to chlorinate benzene, toluene, xylenes, and also to convert carbon bisulfide into carbon tetrachloride. The products, chlorinated by this method, always contain traces of iodine derivatives.[1]

Other chlorine carriers (catalysts) are bromine (not as good as iodine), sulfur, charcoal, bone black, and a series of metallic chlorides: those of iron, aluminum, thallium, molybdenum, antimony, tin, gold, vanadium, uranium and zinc.

Bromine carriers (catalysts) are: Iodine, sulfur, the chlorides of Al, Fe^{III}, and Hg, the requisite being that the halogen salts are free from water. Aluminum amalgam also is a good bromination catalyst.[2]

Iodination is catalyzed in an analogous manner by phosphorus, the chlorides and bromides of Fe^{III} and aluminum, and iodine chloride.[1] Iodination is seldom carried out.

Fluorination[3, 4] is mostly carried out indirectly, to control the violence of the reaction of fluorine with organic compounds. Hydrogen fluoride, HF, has been studied carefully as a fluorinating agent.[3] Acetyl chloride and hydrogen fluoride form acetyl fluoride and hydrogen chloride very rapidly. Acid anhydrides, e.g., acetic anhydride, form with hydrogen fluoride the acid fluoride and the acid. Ethyl alcohol, at 140°C, forms ethyl fluoride.

Benzotrichloride, at 0°C, is converted into benzotrifluoride:[4]

$$C_6H_5 \cdot CCl_3 + 3HF \rightarrow C_6H_5 \cdot CF_3 + 3HCl$$

Hydrogen fluoride also adds to double and triple bonds. Metallic fluorides, such as those of antimony or zinc, act as fluorine carriers (catalysts) to replace chlorine with fluorine in organic compounds, e.g., in the making of dichlorodifluoromethane.[3]

By dechlorinating chlorinated hydrocarbons, using aluminum chloride as a catalyst, oily polymers are obtained which have the properties of lubricating[5] and drying oils.[6]

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[1] Sabatier, P.: *La Catalyse en Chimie Organique,* Librairie Polytechnique, Paris, 1920, p. 103.

[2] Cohen and Dakin: *J. Chem. Soc.,* **75**, 893 (1899).

[3] Simon: *Ind. Eng. Chem.,* **32**, 181 (1940).

[4] Simon et al.: *J. Am. Chem. Soc.,* **54**, 129 (1932); *ibid.,* **55**, 1458 (1933); *ibid.,* **60**, 492, 2267, 2952 (1938); *ibid.,* **61**, 1521, 1795, 1821 (1939).

Boswell and McLaughlin[7] chlorinated methane, using partly reduced cupric chloride on pumice as a catalyst. A yield of 75–80 per cent methyl chloride was obtained, when the ratios of the moist gases were $N_2:CH_4:Cl_2 = 70:7:1$, and a yield of 80 per cent of carbon tetrachloride, when the ratios were $N_2:CH_4:Cl_2 = 7:1:4$.

Kharasch et al.[8] have studied the use of sulfuryl chloride as a chlorinating agent in the presence of organic peroxides, e.g., benzoyl peroxide. The theory is that the sulfuryl chloride acts as a source of chlorine atoms in the presence of the peroxide catalyst, the latter acting by a free radical mechanism as follows:

1. $C_6H_5{\cdot}CO{\cdot}OO{\cdot}CO{\cdot}C_6H_5 \rightarrow 2C_6H_5^- + 2CO_2$
2. $C_6H_5^- + SO_2Cl_2 \rightarrow {}^-SO_2Cl + C_6H_5Cl$
3. ${}^-SO_2Cl \rightarrow SO_2 + Cl^-$
4. $Cl^- + RH \rightarrow R^- + HCl$
5. $R^- + SO_2Cl_2 \rightarrow RCl + {}^-SO_2Cl$

By this method, paraffin hydrocarbons, side chains of aromatic hydrocarbons, aliphatic acids, aldehydes and ketones, etc., can be chlorinated, the general reaction scheme being:

$$RH + SO_2Cl_2 \xrightarrow{\text{organic peroxide}} RCl + SO_2 + HCl$$

The sulfuryl chloride and the catalyst (0.001 to 0.005 mol of catalyst per mol of sulfuryl chloride) are refluxed with the compound to be chlorinated, the reaction being complete when no more gases are given off. Yields of about 80 per cent are very readily obtained, and if the condensation is effective, and the condensate returned to the bulk of the reaction mass, the yields can be made quite quantitative.

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[5] Johnson: British Patent 320,846 (1929).

[6] Gardner and Bielouss: *Ind. Eng. Chem.*, **14**, 619 (1922).

[7] Boswell and McLaughlin: *Can. J. Research*, **1**, 240 (1929).

[8] Kharasch et al.: *J. Am. Chem. Soc.*, **61**, 2142, 3089 (1939); *ibid.*, **62**, 925 (1940).

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Thomas, C. A., M. B. Moshier, H. E. Morris, and R. W. Moshier: *Anhydrous Aluminum Chloride in Organic Chemistry,* Am. Chem. Soc. Monograph, New York, Reinhold Publishing Corp., 1942; Williams and Vaughan: *Halogenation and Hydrohalogenation Reactions by Catalytic Processes,* Twelfth Report of the Committee on Catalysis, National Research Council, New York, John Wiley & Sons, Inc., 1940, p. 240; Symposium on chlorination processes: *Ind. Eng. Chem.,* **33**, 137 (1941); Curme: U. S. Patent 1,422,838 (1922); McKee: U. S. Patent 1,133,049 (1916); McKee and Salls: U. S. Patent 1,765,601 (1930); *Ind. Eng. Chem.,* **16**, 251 (1924); *Woodward Chem. Eng. News,* **22**, 1092 (1944).

10. Alkylation

A large number of compounds of metals and alkyl groups are known; these compounds correspond to the metallic chlorides, from which they are often derived ($Zn(CH_3)_2$, $Sn(C_2H_5)_4$, $Pb(C_2H_5)_4$, etc.). Also well known are the salt-like metal compounds which contain both a halogen and an alkyl group, e.g., $CH_3 \cdot Mg \cdot I$.[1] Friedel and Craft (1877) alkylated aromatic hydrocarbons by the reaction of alkyl halides with aromatic hydrocarbons in the presence of anhydrous $AlCl_3$:[3]

$$C_6H_6 + CH_3Cl \rightleftarrows C_6H_5 \cdot CH_3 + HCl$$

If the reaction is not stopped when the calculated quantity of acid has been evolved, other alkylation products are formed, this being due to the fact that the mono-substituted product reacts with more halide to form a di-substituted one, and this, in turn, forms a tri-substituted product in a similar way. The best yield of the mono-substituted product is obtained by using 15 to 20 per cent of $AlCl_3$ based on the weight of the alkyl chloride.

The reversibility of the reaction is very important. As example shall be named ethylbenzene which, when kept in contact with $AlCl_3$, breaks down into benzene and diethylbenzene.[2] Polyethylbenzenes in benzene with $AlCl_3$, especially in a current of HCl, are converted into ethylbenzene.

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[1] Grignard: *Compt. rend.,* **130**, 1322; *ibid.,* **132**, 336, 558 (1901).

[2] Anschutz and Immendorf: *Ber.,* **17**, 2816 (1884); *ibid.,* **18**, 657 (1885).

[3] Thomas, C. A., N. B. Moshier, H. E. Morris, and R. W. Moshier: *Anhydrous Aluminum Chlorides in Organic Chemistry,* Am. Chem. Sec. Monograph, New York, Reinhold Publishing Corporation, 1942.

Ethylene can be made to react with benzene in the presence of $AlCl_3$ if intensive and rapid stirring is used. A given amount of benzene can, in this way, be reacted with the proper amount of ethylene, and almost complete conversion into ethylbenzene, or into di- up to hexa-ethylbenzene, is obtained. Propylene also reacts with benzene under these conditions.[3a]

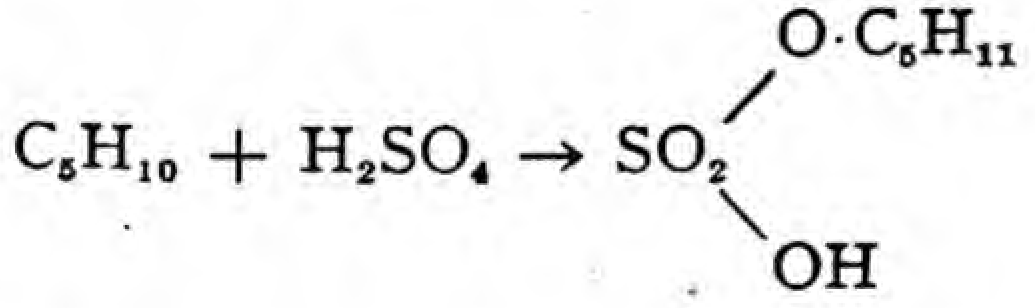
With respect to the use of aluminum chloride in Friedel and Crafts synthesis, Boswell and McLaughlin[5] found that the activity of the $AlCl_3$ is impaired by occluded HCl. It was also found that an approximately equimolecular mixture of the chlorides of Al and Fe^{III} was of higher activity than that of pure $AlCl_3$.

Aliphatic hydrocarbons and aromatic amines may be alkylated directly by ethylene. Saturated hydrocarbons, e.g., hexane, are alkylated by olefins to alkyl-substituted paraffins.[4] Direct alkylation has the advantage that the preliminary preparation of alkyl halides is not necessary. Sulfuric acid causes condensation of olefins with benzene hydrocarbons to give substituted benzenes.[6, 7, 8] Sulfuric acid acts upon a mixture of amylene and benzene at 0°C, causing alkylation of the benzene with the formation of mono-, di-, and tri-amyl benzenes:[8, 8a]

$$C_6H_6 + C_5H_{10} \rightarrow C_6H_5\cdot C_5H_{11}$$

The olefin hydrocarbon forms alkyl sulfate which reacts as follows:[6]

1.



$$C_5H_{10} + H_2SO_4 \rightarrow SO_2\begin{matrix}\diagup O\cdot C_5H_{11}\\ \diagdown OH\end{matrix}$$

[3a] Milligan and Reid: *J. Am. Chem. Soc.*, **44**, 206 (1922); Berry and Reid: *Ibid.*, **49**, 3142 (1927).

[4] Birch and Dunstan: *Trans. Faraday Soc.*, **35**, 1013 (1939).

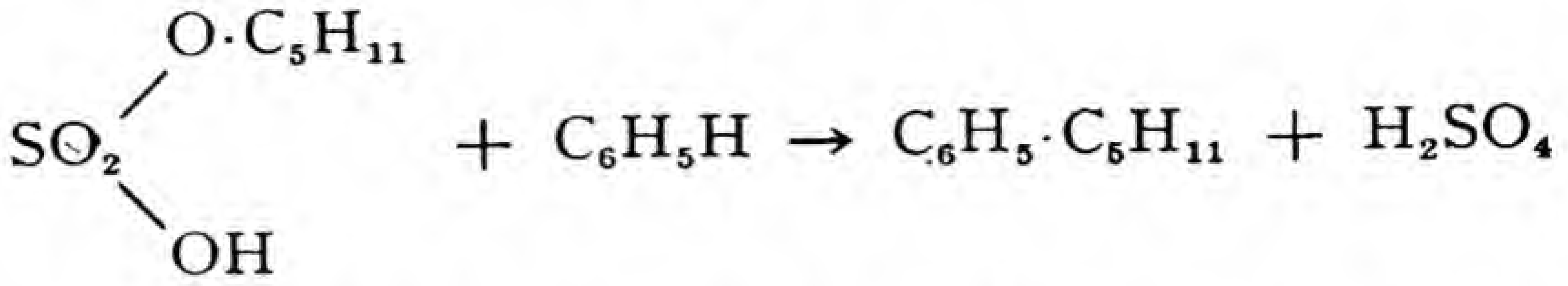
[5] Boswell and McLaughlin: *Can. J. Research*, **1**, 400 (1929).

[6] Spilker: *Ber.*, **23**, 3169 (1890).

[7] Brochet: *Compt. rend.*, **117**, 115 (1893).

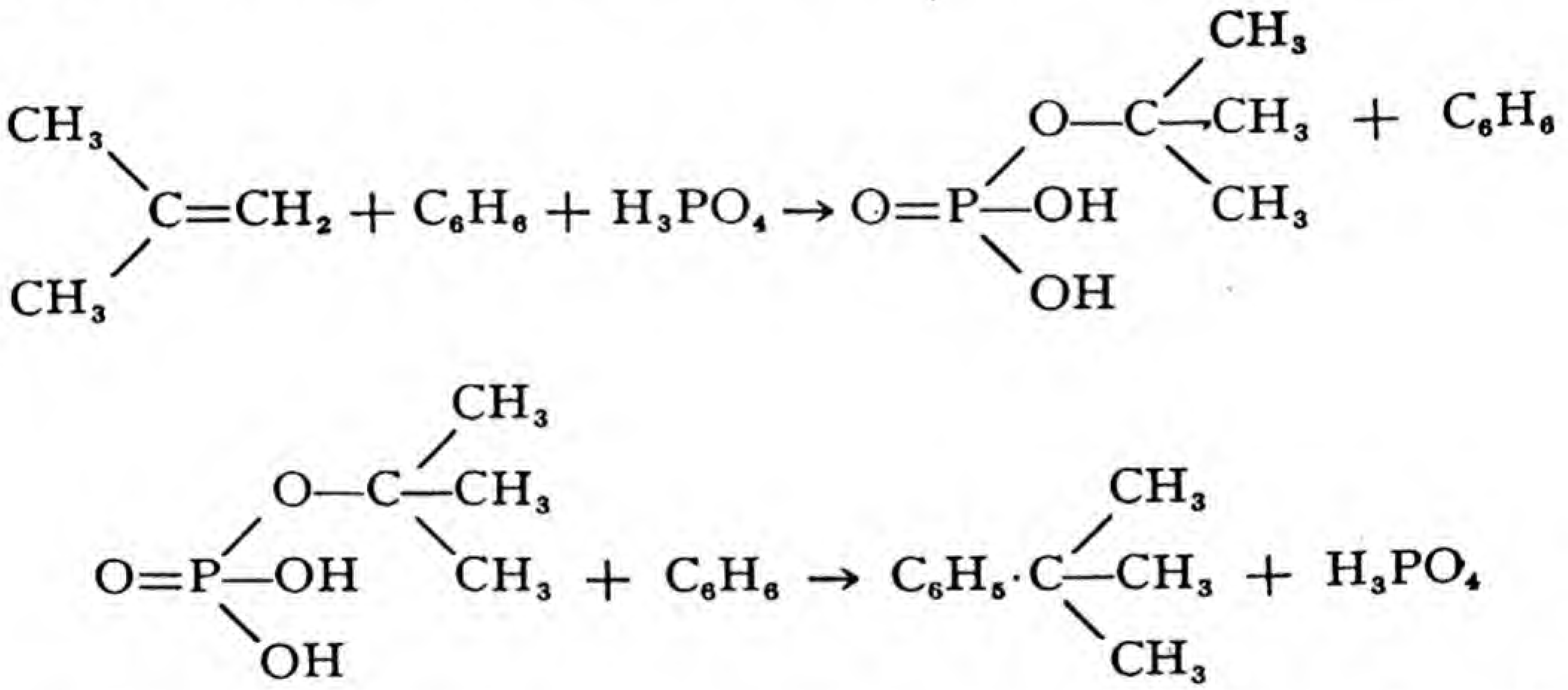
[8] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures*, New York, The Macmillan Company, 1937.

[8a] Ipatieff and Komarewsky: U. S. Patents 2,098,045 and 2,098,046 (1937).

2. 

$$SO_2(O{\cdot}C_5H_{11})(OH) + C_6H_5H \rightarrow C_6H_5{\cdot}C_5H_{11} + H_2SO_4$$

Ipatieff[8] draws the conclusion that polymerization and dehydration catalysts are also alkylation catalysts, the formation of intermediate esters with the catalyst being effected in all cases. Working under pressure and in the presence of perchloric acid, ethylene and amylene alkylated benzene to form ethyl and amyl benzenes respectively. In alkylating benzene by isobutylène at ordinary pressure in the presence of phosphoric acid, it was found that polymerization also took place:[8, 8a]



$$(CH_3)_2C{=}CH_2 + C_6H_6 + H_3PO_4 \rightarrow O{=}P(OH)_2{-}O{-}C(CH_3)_3 + C_6H_6$$

$$O{=}P(OH)_2{-}O{-}C(CH_3)_3 + C_6H_6 \rightarrow C_6H_5{\cdot}C(CH_3)_3 + H_3PO_4$$

This addition of isobutylene to phosphoric acid follows the rule that oxygen combines with the least hydrogenated carbon atom.[8] The use of trialkyl phosphates in alkylation has been discussed by Noller and Dutton,[9] and of phosphorous pentoxide by Malishev.[10]

Phenols alkylate readily with olefins, in the presence of sulfuric[11] or phosphoric[8] acid. According to Ipatieff[8] the reaction with phosphoric acid proceeds as follows:[8, 8a, 15]

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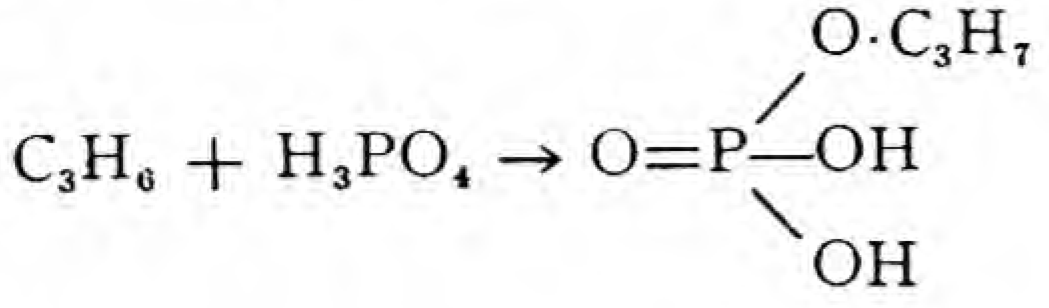
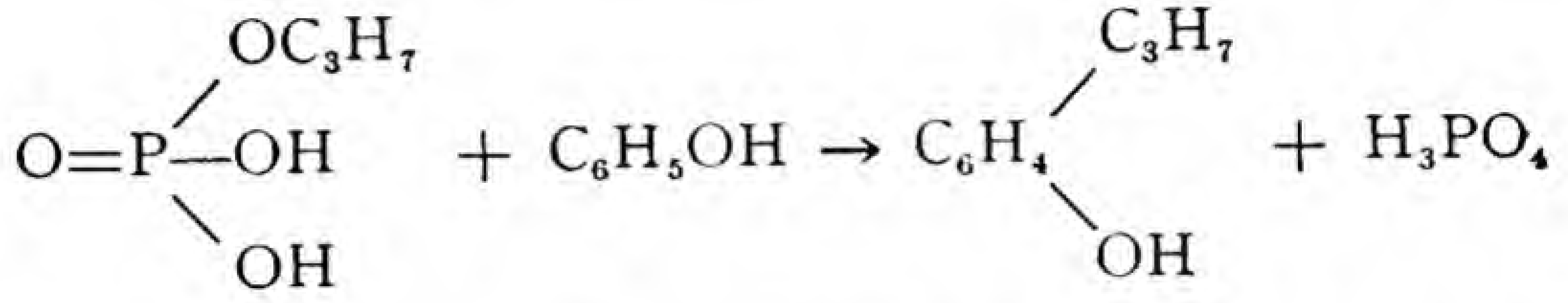
[9] Noller and Dutton: *J. Am. Chem. Soc.*, **55**, 424 (1933).

[10] Malishev: *Ibid.*, **57**, 883 (1935); U. S. Patent 2,141,611 (1938).

[11] Koenigs: *Ber.*, **23**, 3145 (1890).



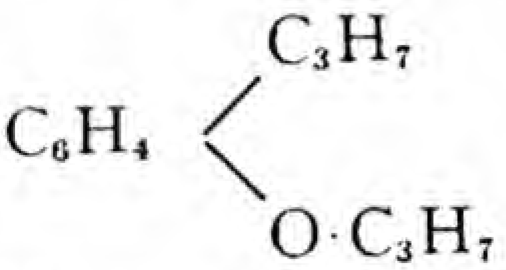
$$C_3H_6 + H_3PO_4 \rightarrow O{=}P\begin{matrix} \diagup O{\cdot}C_3H_7 \\ \!-OH \\ \diagdown OH \end{matrix}$$



$$O{=}P\begin{matrix} \diagup OC_3H_7 \\ \!-OH \\ \diagdown OH \end{matrix} + C_6H_5OH \rightarrow C_6H_4\begin{matrix} \diagup C_3H_7 \\ \diagdown OH \end{matrix} + H_3PO_4$$

Whereas alkylation is the principal reaction, some phenyl ether is formed:[8]

$$C_6H_5OH + C_3H_6 + H_3PO_4 \rightarrow C_6H_5{\cdot}O{\cdot}C_3H_7 + H_3PO_4$$

Also, the ether of an alkylated phenol,  $C_6H_4\begin{matrix} \diagup C_3H_7 \\ \diagdown O{\cdot}C_3H_7 \end{matrix}$ may be formed in small quantity, but it is readily separated from the alkylated phenol by means of NaOH.[8]

Ipatieff[8] discriminates between alkylation and polymerization as effected by the same type of catalyst, i.e., a hydroxylic acid. Polymerization of an olefin is the result of combination of like molecules of the olefin to form one molecule of a hydrocarbon, having a molecular weight which is the multiple of that of the original olefin. Alkylation consists of the combination of unlike hydrocarbon molecules, the resulting compound possessing chemical properties unlike those of the reacting compounds, the molecular weight being the sum of the molecular weights of the reacting compounds.

Higher paraffins and naphthenes can be alkylated by ethylene in the presence of $AlCl_3$ at atmospheric and higher pressure:[8]

$$C_6H_{14} + C_2H_4 \rightarrow C_8H_{18}$$

$$C_6H_{12} + C_2H_4 \rightarrow C_8H_{16}$$

$AlCl_3$ was used in about 10% by weight of the hydrocarbon together with a very small quantity of HCl.

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[12] Ipatieff, Komarewsky, and Grosse: *J. Am. Chem. Soc.*, **57**, 1722 (1935).

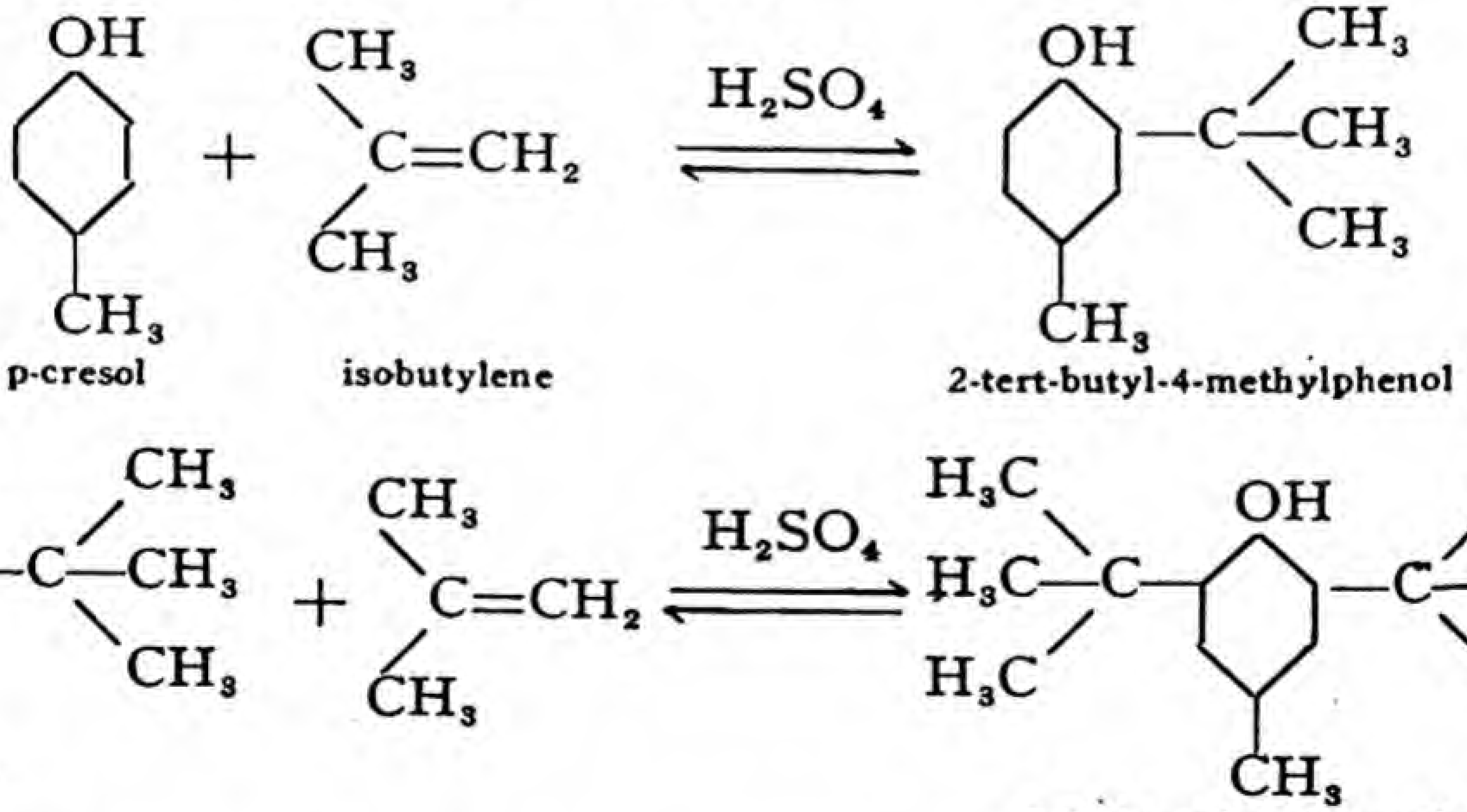
The action of the HCl is explained as follows:[12a]

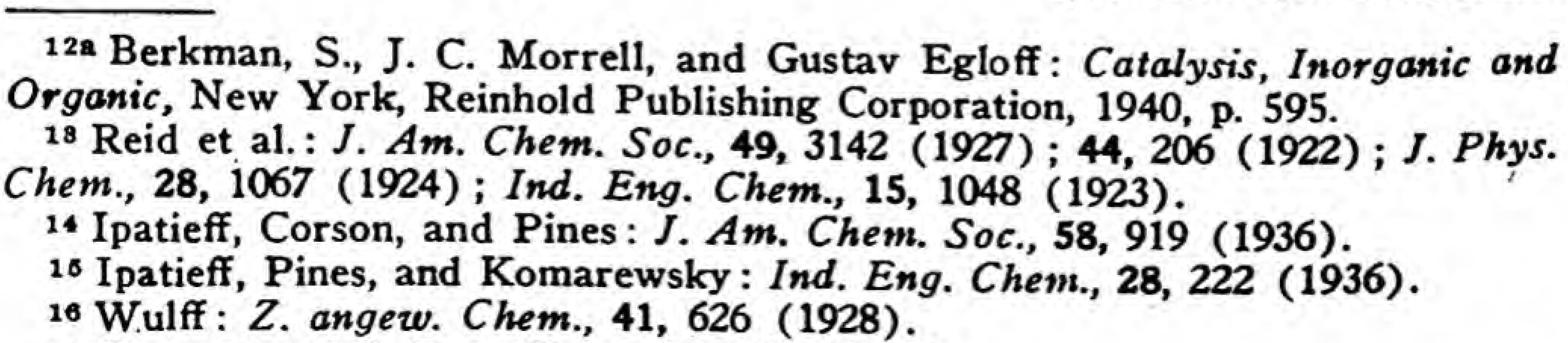
1. $CH_2{=}CH_2 + HCl \rightarrow CH_3CH_2Cl$

2. $C_6H_5{\cdot}H + Cl{\cdot}CH_2{\cdot}CH_3 \xrightarrow{\text{metal chloride}} C_6H_5{\cdot}CH_2CH_3 + HCl$

Alkylated benzene was used for alkylating with ethylene or propylene benzene using $AlCl_3$ as catalyst, by Reid et al., and it was found that the substitution took place readily from mono to hexa positions, the relative amounts of the substituents depending upon the proportion of olefins taken up.[13] Ipatieff, Corson and Pines[14] propylated napthalene to isopropyl-napthalene using 96% sulfuric acid as catalyst; and Ipatieff, Pines and Komarewsky[15] alkylated naphthalene to mono- and di-ethyl naphthalenes using 85% H_3PO_4 as a catalyst (300°C). Wulff[16] used $AlCl_3$ as a catalyst in ethylating naphthalene for making synthetic lubricating oils.

Phenols react selectively with isobutylene in the presence of catalytic amounts of concentrated sulfuric acid to form the corresponding tertiary butyl derivatives:[17]


OH
CH3
H2SO4
C=CH2
CH3
CH3
OH
CH3
C
CH3
CH3
CH3
p-cresol
isobutylene
2-tert-butyl-4-methylphenol


OH
CH3
C
CH3
CH3
CH3
CH3
C=CH2
CH3
H2SO4
H3C
H3C
C
H3C
OH
CH3
C
CH3
CH3
CH3
2,6-di-tert-butyl-4-methylphenol

[12a] Berkman, S., J. C. Morrell, and Gustav Egloff: *Catalysis, Inorganic and Organic,* New York, Reinhold Publishing Corporation, 1940, p. 595.

[13] Reid et al.: *J. Am. Chem. Soc.,* **49,** 3142 (1927); **44,** 206 (1922); *J. Phys. Chem.,* **28,** 1067 (1924); *Ind. Eng. Chem.,* **15,** 1048 (1923).

[14] Ipatieff, Corson, and Pines: *J. Am. Chem. Soc.,* **58,** 919 (1936).

[15] Ipatieff, Pines, and Komarewsky: *Ind. Eng. Chem.,* **28,** 222 (1936).

[16] Wulff: *Z. angew. Chem.,* **41,** 626 (1928).

[17] Weinrich: *Ind. Eng. Chem.,* **35,** 264 (1943).

The following halides have been tried out as catalysts in alkylation reactions: $BeCl_2$, $TiCl_4$, $ZrCl_4$, $HfCl_4$, $ThCl_4$, $NbCl_5$, BF_3, and $TaCl_5$.[12a] In ethylation of benzene with ethylene in the presence of these catalysts, a mixture of mono- and poly-substitutes resulted. $ZrCl_4$ was equal to or better than $AlCl_3$ and $TaCl_5$ just as good. $BeCl_2$ was active at higher temperatures only (200°C).[18]

However, there is some variation in the sequence of the different halide catalysts as published by various investigators.[12a, 19] Burk[19] has tabulated the activity of the halide catalysts on the basis of an extensive reference study, the order of decreasing activity being as follows:

$AlBr_3 > AlCl_3 > FeCl_3 > ZrCl_4 > TaCl_4 > BF_3 > UCl_4 > TiCl_3 > WCl_6 > CbCl_5 > ZnCl_2 > (Sn) > TiCl_4 > BeCl_2 > SbCl_5 > HgCl_2 > Cu_2Cl_2 > BiCl_3 > AsF_3$. Co, Cr, and Mo showed some activity, but the evaluation was uncertain.

Burk concludes from his study that there is evidence that acids of the type of $HAlCl_4$ are involved in halide catalysis, probably through intermediate compound formation.

Besides the capability of $AlCl_3$ of alkylating all classes of hydrocarbons with olefins, it is also able to decompose high-molecular-weight hydrocarbons.[8]

By decomposing hexane, at high temperature, with $AlCl_3$, the resulting product contains gas and also a liquid of higher boiling point than the original hexane.[21] The conclusion is that aluminum chloride splits the molecule of hexane into saturated and unsaturated molecules, and effects the alkylation of undecomposed hexane with olefins in statu nascendi, causing the growth of radicals upon the hexane skeleton:

$$C_6H_{14} \rightarrow C_4H_{10} + C_2H_4$$
$$C_6H_{14} + C_2H_4 \rightarrow C_6H_{13}\cdot C_2H_5$$

---

[18] Kurbatow (Universal Oil Products Company), Berkmann, Morrell and Egloff: *Catalysis, Inorganic and Organic,* New York, Reinhold Publishing Corporation, 1940.

[19] Burk, R. E.: *Halide Catalysts,* Twelfth Report of the Committee on Catalysis, National Research Council, New York, Wiley and Sons, Inc., 1940.

[21] Ipatieff and Dovgelewitch: *Ber.,* **44,** 2987 (1911).

By this process, it is possible to decompose hydrocarbons in the presence of other hydrocarbons which are not susceptible to this treatment, but which will be alkylated by the olefins resulting from the decomposition.

Ipatieff and his associates term alkylation, which takes place after the hydrocarbon molecule has been decomposed, as destructive alkylation. If the decomposed hydrocarbon alkylates itself, the term auto-destructive alkylation is used.[8]

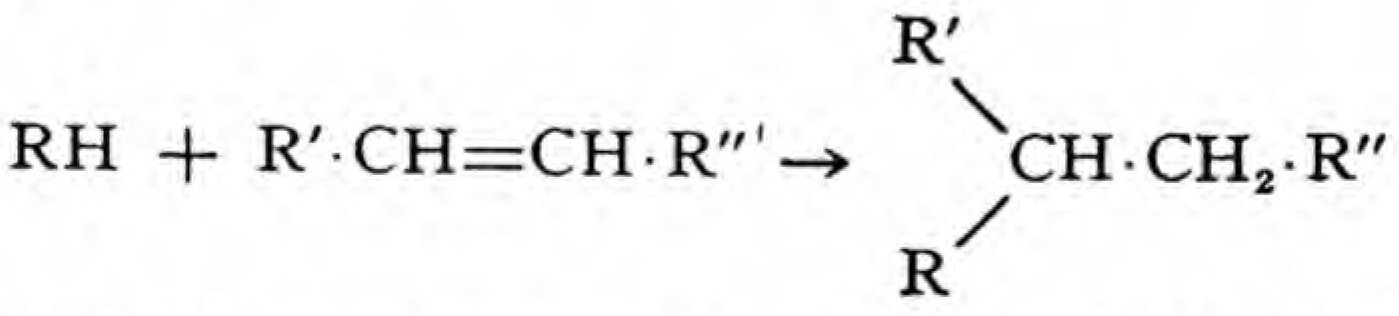
Simons [22] reports that hydrogen fluoride is a suitable catalyst for the preparation of simple organic compounds in good yields and without the formation of appreciable amounts of unwanted polymers.

1. With alkyl halides (including aromatic compounds):

$$RH + R'X \rightarrow R\cdot R' + HX$$

R′ is almost any alkyl radical, and X may be chlorine, bromine, or iodine.

2. With olefins:



$$RH + R'\cdot CH{=}CH\cdot R'' \rightarrow \begin{array}{ll} R' & \\ & \diagdown \\ & \quad CH\cdot CH_2\cdot R'' \\ & \diagup \\ R & \end{array}$$

This reaction takes place readily, usually at 0°C, with relatively small amounts of catalyst.

3. With alcohols:

$$RH + R'OH \rightarrow R\cdot R' + H_2O$$

More hydrogen fluoride is required in this reaction because the alcohol adds to the HF, and it is diluted by the water formed. Tertiary alcohols react most readily, primary alcohols least.

4. With esters:

$$RH + R'\cdot COOR'' \rightarrow R\cdot R'' + R'COOH$$

This reaction takes place readily at 100°C.

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[22] Simons: *Ind. Eng. Chem.*, **32**, 179 (1940).

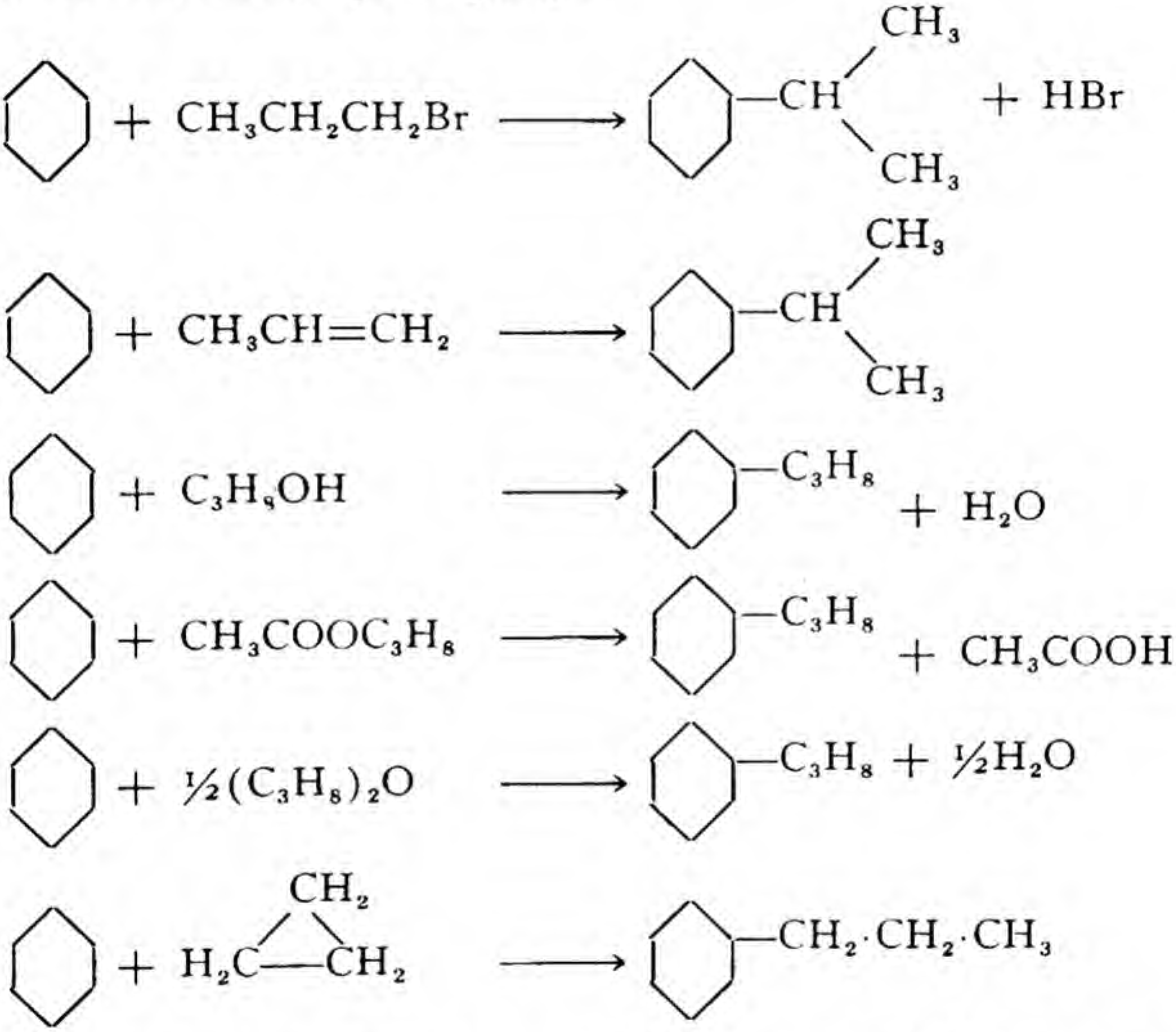
5. With ethers:

$$RH + R'{\cdot}O{\cdot}R'' \rightarrow R{\cdot}R'' + R'OH$$

$$RH + R'OH \rightarrow R{\cdot}R' + H_2O$$

The temperatures required and the extent of the second reaction depend on the reactivity of the R′ and R″ groups. In general, the reactions follow the course of the reactions of alcohols.

6. With benzene (examples):


+ CH₃CH₂CH₂Br
—CH
CH₃
CH₃
+ HBr
+ CH₃CH=CH₂
—CH
CH₃
CH₃
+ C₃H₉OH
—C₃H₈
+ H₂O
+ CH₃COOC₃H₈
—C₃H₈
+ CH₃COOH
+ ½(C₃H₈)₂O
—C₃H₈ + ½H₂O
CH₂
+ H₂C—CH₂
—CH₂·CH₂·CH₃

The methods of alkylation, used in the motor fuel industry, are mentioned elsewhere (page 379). However, these reactions are so important that they should be mentioned here briefly. The reaction mechanism involved has been discussed by Birch and Dunstan [4] who used sulfuric acid as a catalyst in the reaction between isoparaffins and olefins. Isobutane, isopentane and isohexane (2-methylpentane) react readily, but isooctane (2,2,4-trimethylpentane) cannot be alkylated by this process. The olefins investigated were propene, butene-1 and butene-2, isobutene and its di- and trimerides, the butene-isobutene codimer and trimethylethylene. All of these compounds react readily giving excellent yields of isoparaffinic compounds. The resulting products are complex mixtures of isoparaffins chiefly boiling in the range of the gasoline compounds, i.e., from 27 to 185°C; the remainder is a small residue of isoparaffins of high boiling point, together with an even smaller amount of olefins.

In discussing the possible reaction mechanism, the assumption is made that fission of the primary product can, in certain instances, take place at more than one position of the molecule. Evidence for this is the fact that similar isoparaffins are formed from various pairs of reactants. Based on this thought, the following reaction scheme is presented:

$$\begin{tikzcd}
C_4H_8 + \mathrm{iso}C_4H_{10} \arrow[r, phantom, "\rightleftarrows"] & (CH_3)_3C\cdot CH_2\cdot CH(CH_3)_2 \arrow[dl, shift right] \\
C_3H_6 + \mathrm{iso}C_5H_{12} \arrow[ur, shift right] &
\end{tikzcd}$$

$$\mathrm{iso}C_5H_{12} + C_4H_8 \rightleftarrows (CH_3)_3C\cdot CH_2\cdot CH_2\cdot CH(CH_3)_2 \rightleftarrows C_3H_6 + \mathrm{iso}C_6H_{14}$$

$$C_3H_6 + \mathrm{iso}C_4H_{10} \rightleftarrows \left\{\begin{matrix} (CH_3)_2\cdot CH\cdot CH_2\cdot CH(CH_3)_2 \\ (CH_3)_2CH\cdot CH(CH_3)\cdot CH_2\cdot CH_3 \end{matrix}\right.$$

$$C_3H_6 + \mathrm{iso}C_5H_{12} \rightleftarrows \left\{\begin{matrix} (CH_3)_2CH\cdot CH_2\cdot CH_2\cdot CH(CH_3)_2 \\ (CH_3)_2CH\cdot CH_2\cdot CH(CH_3)CH_2CH_3 \end{matrix}\right.$$

The products formed in various olefin-isoparaffin alkylation reactions are as follows:

Isoparaffin	Olefin	Main product formed
Isobutane	Propene	2,4-, 2,3-dimethylpentane 2,2,4-trimethylpentane 2;3-dimethylbutane

Isoparaffin	Olefin	Main product formed
Isobutane	Butene-1 Butene-2 Diisobutene	2,2,4-trimethylpentane 2,5-, 2,4-dimethylhexane 2,2,5-trimethylhexane 2,3-dimethylbutane 2-methylpentane (2,2,6-trimethylheptane ?) Isopentane
Isopentane	Propene	2,3-, 2,4-, 2,5-dimethylhexane Isobutane
Isopentane	Butene-2 Diisobutene	2,2,5-trimethylhexane Isohexanes (probably mainly 2-, 3-methylpentanes) (2,2,6-trimethylheptane ?)
2-Methylpentane	Butene-2 Diisobutene	(2,2,6-trimethylheptane ?) Isobutane Isopentane

GENERAL REFERENCES

Radzievanowski: *Ibid.*, **27**, 3255 (1894); Pardee and Dodge: *Ind. Eng. Chem.*, **35**, 273 (1943); Komarewsky: *J. Am. Chem. Soc.*, **59**, 2715 (1937).

11. Isomerization

It is well known that isomerization reactions may take place under the influence of heat alone, but the temperature required for the intramolecular rearrangement is lowered considerably in the presence of suitable catalysts.[1, 2]

The isomerization equilibrium is between two molecules only, the equilibrium constant, K, being determined according to the law of mass action: $c_B/c_A = K$.[1a]

The equilibrium in a gaseous isomerization reaction:

$$A_{(gas)} \rightarrow M_{(gas)}$$

---

[1] Egloff, Gustav, G. Hulla, and V. J. Komarewsky: *Isomerization of Pure Hydrocarbons*, Am. Chem. Soc. Monograph, New York, Reinhold Publishing Corp., 1942.

[1a] Broensted, J. N.: *Physical Chemistry*, London, William Heinemann, Ltd., 1939, p. 165.

[2] Aston: *Ind. Eng. Chem.*, **34**, 514 (1942).

is expressed by

$$K = \frac{P_M\gamma_M}{P_A\gamma_A} = \rho\frac{\gamma_M}{\gamma_A} = \frac{x}{100-x}\cdot\frac{\gamma_M}{\gamma_A}$$

where ρ is the ratio of mols of M to mols of A in the equilibrium mixture, x is the percentage yield of isomer M, and γ_M and γ_A are the fugacities of the two isomeric gases. At ordinary pressures, γ_M and γ_A are close to unity, thus the yield cannot be changed by pressure. At high pressure, changes in x can be produced only by the small variation in γ caused by the change of pressure. For calculation of K, see Aston's paper.[2]

In discussing isomerism in hydrocarbons, Egloff, Hulla, and Komarewsky [1] state that in raising the temperature from zero upwards, atoms and electrons become more and more mobile, and no hydrocarbon can be considered absolutely stable.

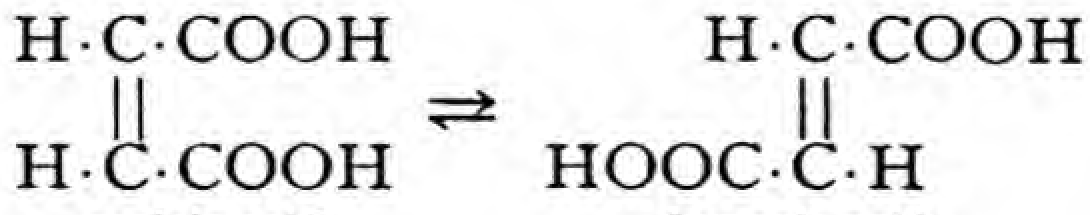
If the heat of formation of a hydrocarbon isomer is H_T°, the freedom of motion of the atoms of the isomer is TS_T° (i.e., the product of the entropy and absolute temperature in degree Kelvin), then the free energy change in kilogram calories at 15°C per mol per centigrade degree is calculated as follows:

$$\Delta F_T^\circ = \Delta H_T^\circ - T\Delta S_T^\circ = RT\ \mathrm{Log}_e\ K_{equil.}$$

$$K_{equil.} = \mathrm{Antilog}_e\left(-\frac{\Delta H_T^\circ}{RT} + \frac{\Delta S_T^\circ}{R}\right) = \frac{\text{fugacity of final isomer}}{\text{fugacity of remaining isomer}}$$

The equilibrium constant is approximately equal to the rate of partial pressures at moderate total pressure.

A well known isomerization reaction is the transformation of maleic acid to fumaric acid, which is catalyzed by halogen acids,[3] hydrogen ions,[4] or sodium thiosulfate: [5]



$$\begin{matrix} H\cdot C\cdot COOH \\ \| \\ H\cdot C\cdot COOH \end{matrix} \rightleftarrows \begin{matrix} H\cdot C\cdot COOH \\ \| \\ HOOC\cdot C\cdot H \end{matrix}$$

maleic acid fumaric acid

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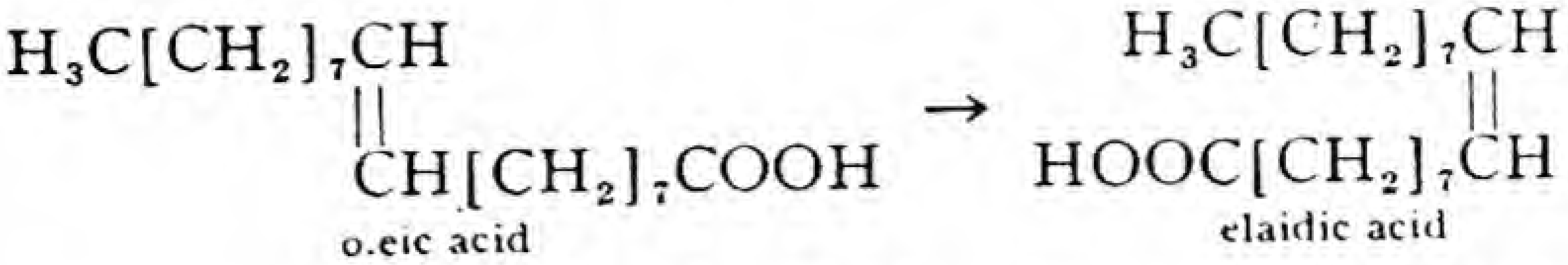
[3] Kekulé: *Liebigs Ann. Chem.* (suppl. vol.) **1**, 133 (1861); Kekulé and Strecher: *Ibid.*, **223**, 186 (1884).

[4] Horrex: *Trans. Faraday Soc.*, **32**, 570 (1937).

[5] Taube: *J. Am. Chem. Soc.*, **65**, 526 (1943).

Oleic acid is isomerized to elaidic acid with nitrous acid [6] or SO_2 [6a] as catalyst:



$$\underset{\text{oleic acid}}{\begin{matrix} H_3C[CH_2]_7CH \\ \| \\ CH[CH_2]_7COOH \end{matrix}} \rightarrow \underset{\text{elaidic acid}}{\begin{matrix} H_3C[CH_2]_7CH \\ \| \\ HOOC[CH_2]_7CH \end{matrix}}$$

The displacement of the double bonds in unsaturated triglycerides has been studied by several workers,[7, 8, 9] and due to the importance of such isomerisms on the quality of hydrogenated vegetable and animal oils and fats, this type of isomerization is of considerable interest.

Bradley and Richardson [9] studied the saponification of drying and semi-drying oils with caustic alkalies, and found that the unsaturated linkages tend to shift their position permanently. The fatty acids and an aqueous solution of alkali were charged in a hydrogenation bomb, rocked, and heated to 225°C for a certain length of time, and then cooled. The soaps were hydrolyzed at 90–95°C with an excess of forty per cent hydrochloric acid or sulfuric acid, the fatty acids being washed free from mineral acids and dried over calcium chloride, or by heating in a current of carbon dioxide at 120°C. Some of the data obtained are presented in the following tables:

Typical Conjugation Assays of Raw Oils
(Bradley and Richardson) [9]

	Percent acids with conjugated double bonds		
	Two	Three	Four
Castor	0.23	0.024	0.0025
Chia	0.30	0.035	0.015
Corn	0.48	0.16	0.0025
Cottonseed	0.41	0.06	0.0
Dehydrated castor	28.4	0.19	0.0
Linseed	0.69	0.12	0.04
Oiticica	0.0	75.8	0.36
Olive	0.40	0.024	0.0

---

[6] Terry, E. M. and L. Eichelberger: *J. Am. Chem. Soc.*, **47**, 1067, 1402 (1925).

[6a] Vlodrop: *Chem. Weekblad,* **38,** 150 (1941); *Chem. Abstracts,* **36,** 5663 (1942).

[7] Moore: *J. Chem. Soc.*, **38**, 320T (1919).

[8] Hilditch and Vidyarthi: *Proc. Roy. Soc. (London)*, A, **122**, 552 (1929).

[9] Bradley and Richardson: *Ind. Eng. Chem.*, **34**, 237 (1942).

Typical Conjugation Assays of Raw Oils (Bradley and Richardson)[9]

	Percent acids with conjugated double bonds		
Peanut	0.30	0.04	0.003
Perilla	0.53	0.19	0.06
Sardine	0.66	0.05	0.02
Soybean	0.79	0.12	0.02
Tung	0.0	84.5	0.38

NB. These figures are based upon the assumption that all observed absorption for each oil is due to conjugation.

Isomerization Experiments (Bradley and Richardson)[9]

Fatty acids		Alkali		Water	Heating		Analysis of recovered acids	
Name	Grams	Name	Grams	Grams	Hours	°C	Two double bonds	Three double bonds
Linseed	75	KOH	75	100	2	225	34.6	7.66
Linseed	75	NaOH	75	125	3	225	41.0	8.20
Soy	100	KOH	75	110	2½	225	20.2[c]	1.33
Sardine[a]	75	LiOH	100	100	3½	225	23.2	8.00
Dehydrated castor[b]	75	LiOH	75	100	3	225	41.7	0.75

[a] Isomerization also produced 2.3% of an acid containing four conjugated double bonds.

[b] The original acids, typical of those made commercially from dehydrated castor oil, contained 26.0% of two-double-bonded, and 0.27% of three-double-bonded conjugated acids.

[c] This value was doubled in succeeding experiments.

The quantitative estimation of each of the several forms of conjugation was made by means of ultraviolet absorption spectra.

The isomerization of hydrocarbons has been studied widely, and special attention is called to the pioneering work by Ipatieff et al.,[10, 11] and the recent monograph "Isomerization of Pure Hydrocarbons" by Egloff, Hulla, and Komarewsky.[1]

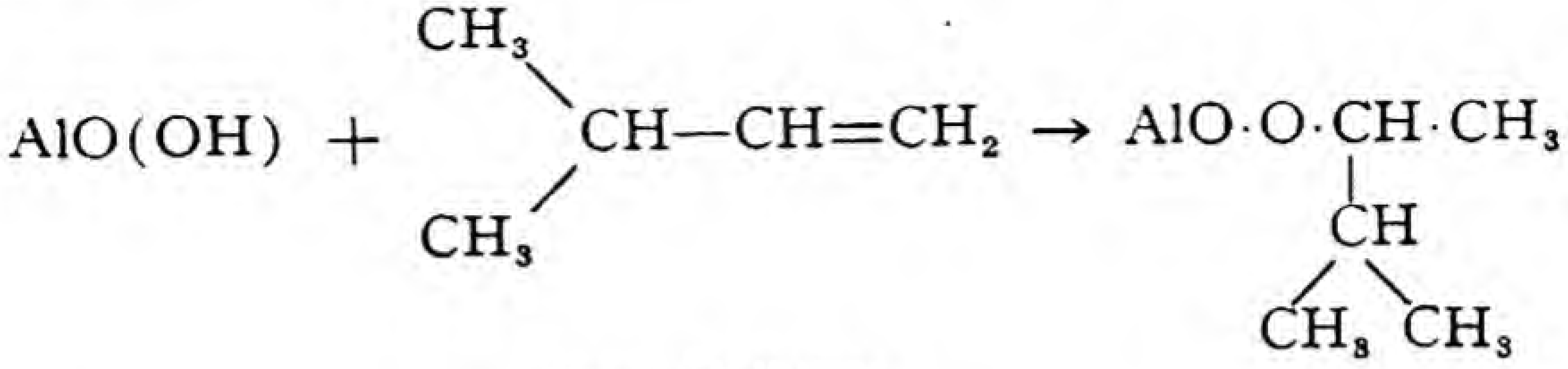
The isomerization of straight-chain alkanes, in the hydrocarbons of gasoline, to branched-chain hydrocarbons of higher anti-knock value is of immense practical interest in the production of high-grade motor fuels (see page 360).

A very interesting theory has been derived, regarding the catalytic isomerization mechanism in hydrocarbons, by Ipatieff,[10] who used alumina as a catalyst for isomerizing isopropyl ethylene into ethyl ethylene and assumed formation of intermediate esters of the hydrocarbon with alumina hydrate in interpreting the reaction:[10]

---

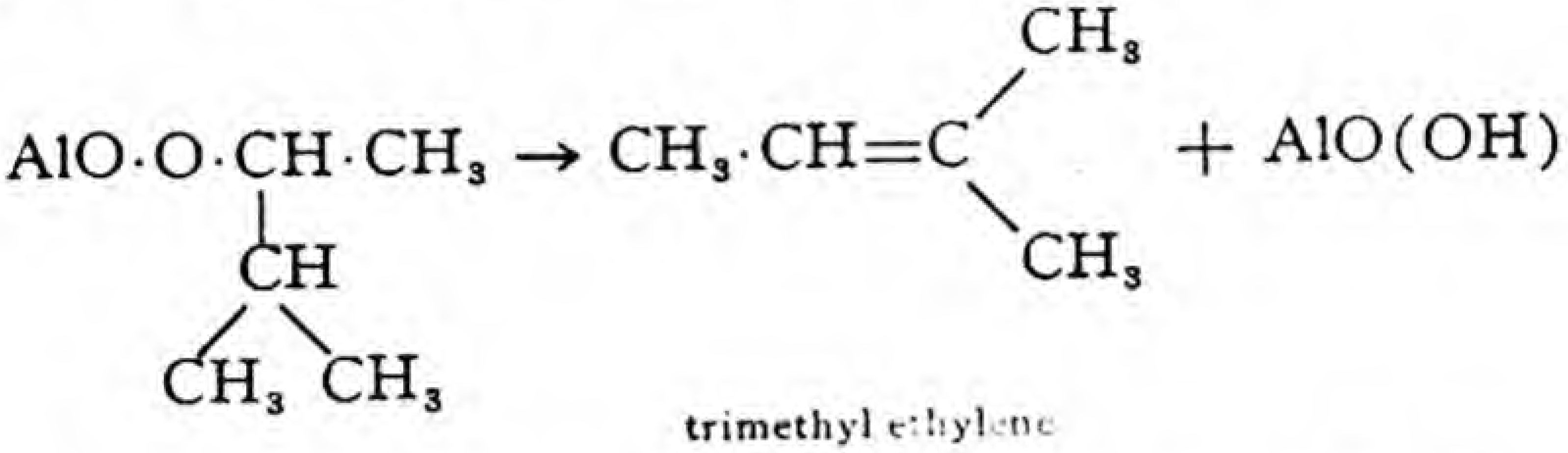
[10] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures*, New York, The Macmillan Company, 1937, p. 126.

[11] Ipatieff and Leontovitch: *Ber.*, 36, 2016 (1903).



isopropyl ethylene

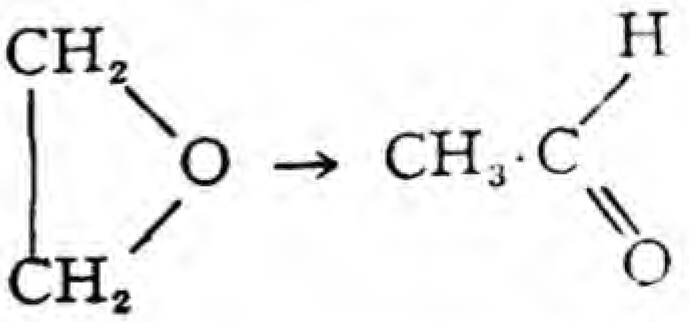
and by decomposition of this ester:



trimethyl ethylene

From this and many other examples by Ipatieff, the general rule is drawn that the addition of an olefin to an acid, to form an ester, proceeds in such a way that an atom of oxygen combines with the carbon atom which is least hydrogenated.

Ipatieff distinguishes between ordinary isomerization in which the chemical function of the isomer molecule is unchanged; and isomerization in which there is change in the chemical function, the latter change being termed metameric catalytic transformation. An example is the catalytic metameric transformation of ethylene oxide into acetaldehyde with alumina as a catalyst:



Isomeric change is undoubtedly of immense importance in chemical reaction mechanisms and particularly in contact catalysis, the function of the catalyst, in part, undoubtedly being to bring about such intramolecular changes that the molecule becomes reactive (Lohse).

GENERAL REFERENCE

Werner, A.: *Lehrbuch der Stereochemie*, Jena, Gustav Fischer, 1904.

12. Condensation

With the tremendous advancement of industrial synthesis of chemicals as well as of plastics and resins, condensation reactions have achieved great industrial importance.

In condensation reactions, different organic molecules combine, often with the elimination of water or hydrochloric acid. The difference between condensation and polymerization reactions is not well defined, and in some cases, it is difficult to draw the line.

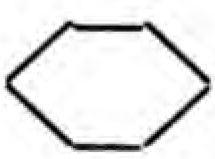
Fischer and Tropsch[1] synthesize olefinic hydrocarbons from water-gas and then condense these with $AlCl_3$; or they chlorinate the fractions and then condense these, alone or with other aromatic hydrocarbons (e.g., xylene), according to the procedure of Friedel and Crafts. By this process, lubricating oils are made from water-gas. (See also page 329.)

Cinnamic acid is formed by condensation of benzaldehyde with malonic acid, piperidine being used as a catalyst:[2]

I. In the cold: $C_6H_5{\cdot}CHO + CH_2(COOH)_2 +$

$$HN{=}C_5H_{10} \rightarrow C_6H_5CH(NC_5H_{10})CH(COOH)_2$$

II. By heating: $C_6H_5CH(NC_5H_{10})CH(COOH)_2 \rightarrow$



$$CH{=}CH{\cdot}COOH + CO_2 + HN{=}C_5H_{10}$$

The condensation of o-benzoylbenzoic acid in sulfuric acid to anthraquinone[3] is accelerated by the presence of sulfur trioxide. The reaction is unimolecular and practically quantitative. It is inhibited by the water and, to a greater extent, by the anthraquinone formed during the reaction. The energy of activation, in the fuming sulfuric acid medium, is 26,100 calories, and the temperature coefficient for a 10°C rise is approximately 3.

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[1] Fischer and Tropsch: *Ber.*, **59**, 830, 832, 923 (1926).

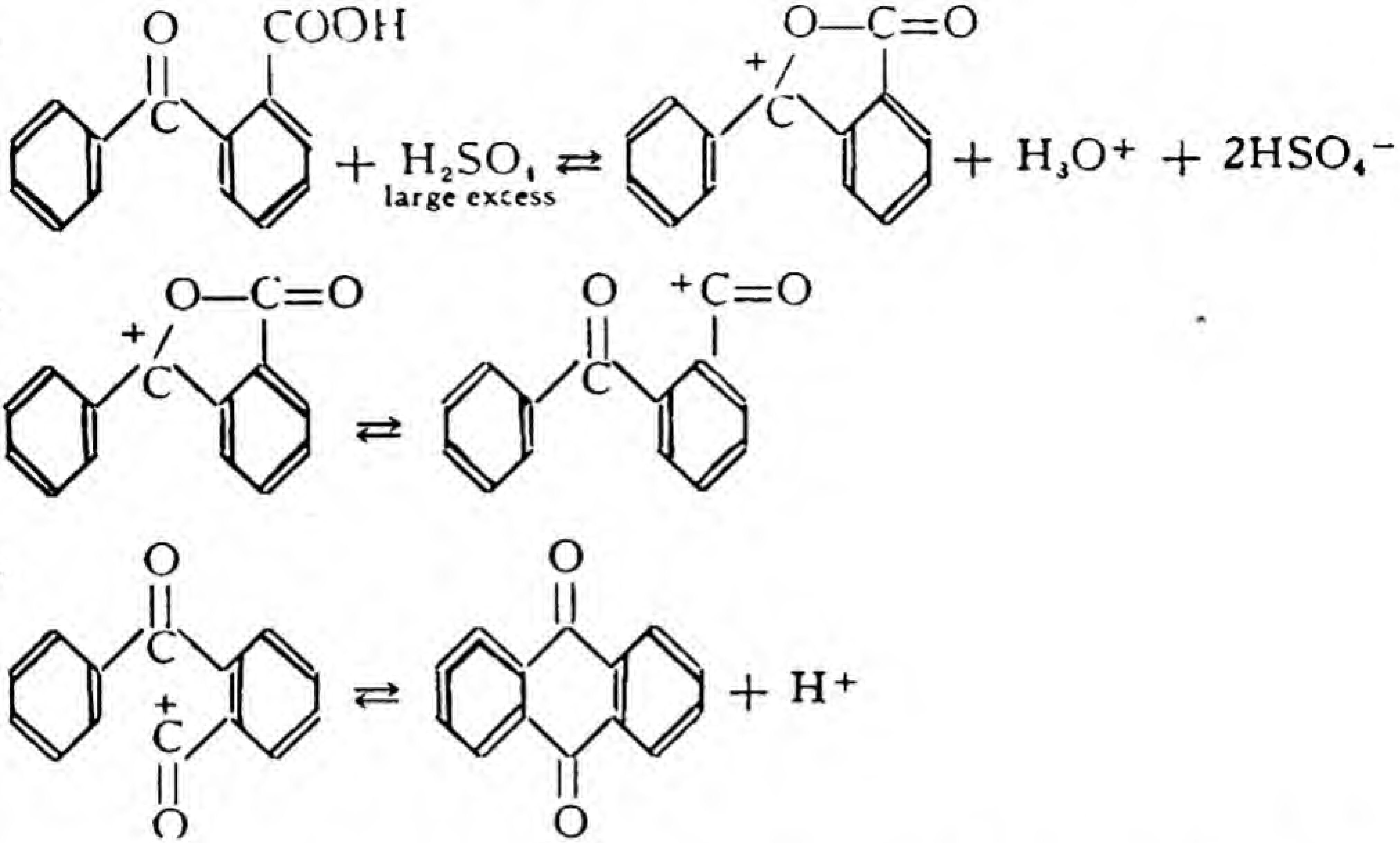
[2] Rodinov: *J. Am. Chem. Soc.*, **51**, 841, 847 (1929).

[3] Deane and Huffmann: *Ind. Eng. Chem.*, **35**, 684 (1943).

1.

2.

3.



Unsaturated methylketones are synthesized by reaction of branched-chain olefins with acetic anhydride in the presence of zinc chloride or sulfuric acid as catalysts:[4]

$$C_nH_{2n} + (RCO)_2O \rightarrow C_nH_{2n-1}COR + RCOOH$$

Diisobutylene and acetic anhydride yield methyl octenyl ketone (4,6,6-trimethyl-3-heptane-2-one):

$$C_8H_{16} + (CH_3CO)_2O \rightarrow C_8H_{15}CO{\cdot}CH_3 + CH_3COOH$$

Optimum yield is obtained when using less than one mol of condensing agent per mol of reactants.

Ipatieff[5, 6] reports a considerable number of condensation reactions and accounts in a detailed way for the mechanisms involved. As an example serves the condensation of ethyl alcohol heated with alumina at 530–540°C for six hours. The mechanisms involved are as follows:

---

[4] Byrns and Doumani: *Ind. Eng. Chem.*, **35**, 349 (1943).

[5] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures*, New York, The Macmillan Company, 1937, p. 441.

[6] Ipatieff and Razuvaev: *Ber.*, **59**, 306, 2031 (1926).

a. $CH_3CHO + CH_3CHO \rightarrow CH_3CH(OH){\cdot}CH_2{\cdot}CHO$

b. $CH_3CHO + CH_3CHO \rightarrow CH_3CH(OH)CO{\cdot}CH_3$

c. $CH_3CHO + CH_3CHO \rightarrow CH_3COO{\cdot}CH_2{\cdot}CH_3 + H_2O \rightarrow$
$CH_3CH_2OH + CH_3COOH$

The aldol, formed at a high temperature, decomposes as follows:

$$CH_3CH(OH)CH_2CHO \rightarrow \underset{\text{isopropyl alcohol}}{CH_3CH(OH)CH_3}$$

By using an iron catalyst, isopropyl alcohol decomposes into acetone and hydrogen:

$$CH_3CH(OH)CH_3 \rightarrow CH_3COCH_3 + H_2$$

The reaction may also proceed over acetic acid with alumina at a higher temperature:

$$2CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O$$

For further details, the original text should be consulted.

The primary and secondary nitroparaffins combine with formaldehyde in the presence of an alkaline condensing catalyst such as sodium carbonate. The number of mols of formaldehyde, which can be combined with a nitroparaffin, is equal to the number of hydrogen atoms which are attached to the same carbon atom as is the nitro group. Consequently, nitromethane can react with three molecules of formaldehyde, nitroethane and 1-nitropropane with two, and 2-nitropropane with one:[8]

1. $CH_3{\cdot}NO_2 + 3HCHO \rightarrow (CH_2OH)_3C{\cdot}NO_2$
2. $CH_3CH_2NO_2 + 2HCHO \rightarrow (CH_2OH)_2CNO_2{\cdot}CH_3$
3. $CH_3CH_2CH_2{\cdot}NO_2 + 2HCHO \rightarrow (CH_2OH)_2CNO_2{\cdot}CH_2CH_3$
4. $(CH_3)_2CH{\cdot}NO_2 + HCHO \rightarrow (CH_2OH)CNO_2(CH_3)_2$

Higher aliphatic aldehydes can also be condensed with nitroparaffins, but only one molecule will react, regardless of which nitroparaffin is used. Aromatic aldehydes give similar reactions.

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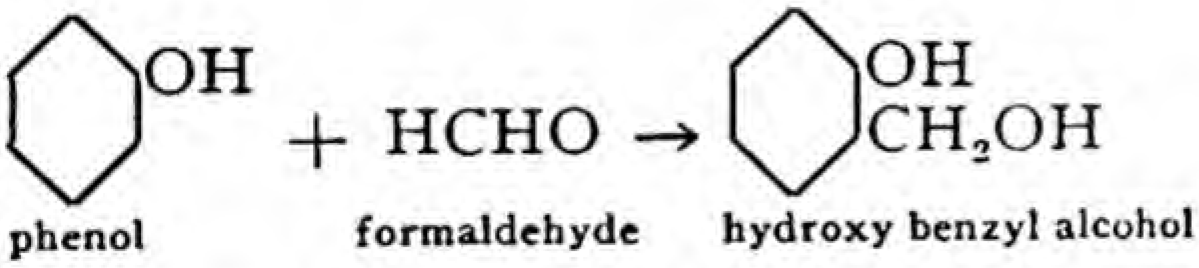
[8] Gabriel: *Ind. Eng. Chem.*, **32,** 887 (1940).

Aldol condensations yield nitrohydroxy compounds in which the hydroxy radical is attached to a carbon atom adjacent to the one with which the nitro group is combined. This rule holds for both nitroglycols and nitroalcohols.

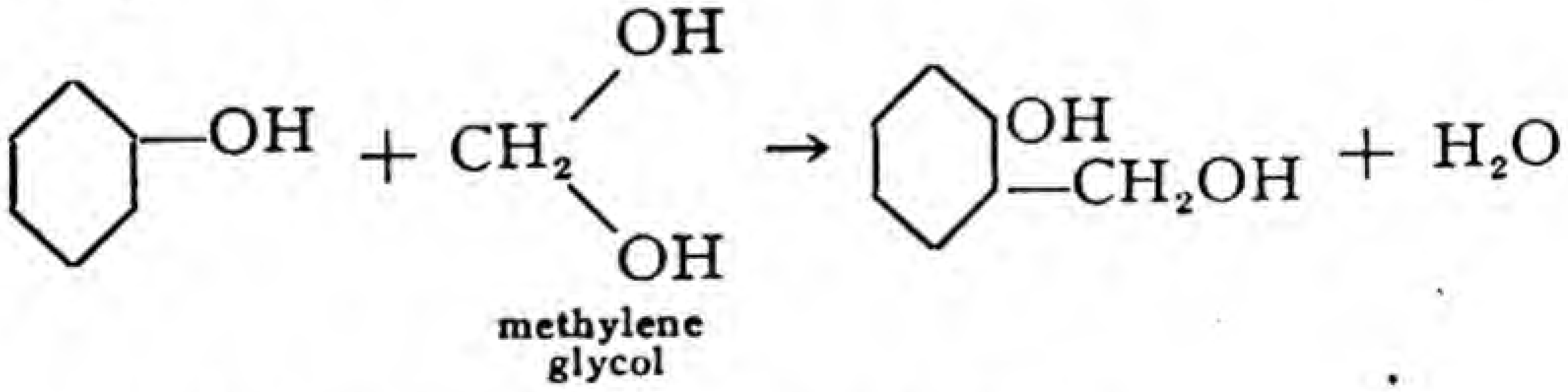
Ipatieff and Pines studied the condensation of ketones and other compounds, e.g., cyclohexanone, cyclohexanol, ethyl ether, with phenol in the presence of phosphoric acid.

A large industrial field has been developed on the basis of fundamental studies of condensation reactions, the results having practical applications in the production of numerous useful chemicals, resins, and plastics.

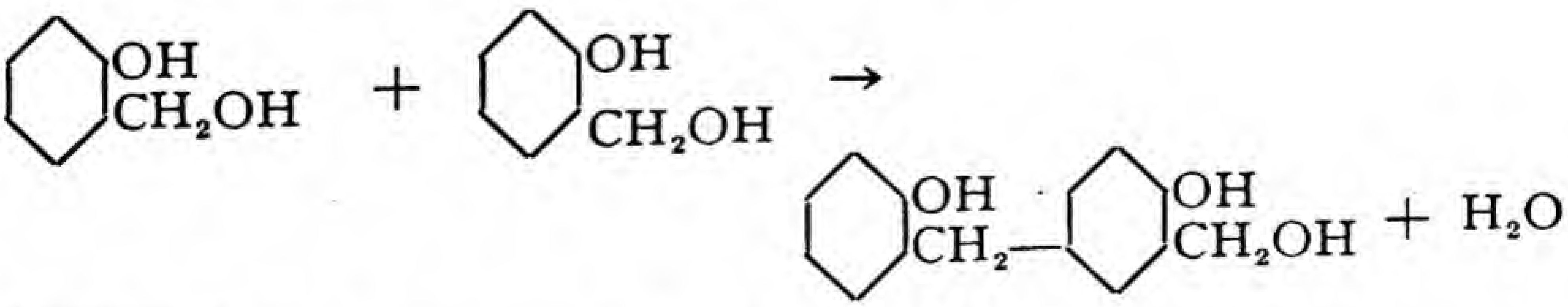
Phenols and aldehydes condense to form resinous products of immense commercial importance (Bakelite, Durez, Resinox, etc.):[9, 10, 11]


OH
+ HCHO →
OH
CH₂OH
phenol
formaldehyde
hydroxy benzyl alcohol

Actually, the formaldehyde is hydrated to methylene glycol [$CH_2(OH)_2$], the reaction with the 40% formaldehyde of the trade being:


—OH
+ CH₂
OH
OH
methylene glycol
→
OH
—CH₂OH
+ H₂O

The phenol-alcohols condense as follows:


OH
CH₂OH
+
OH
CH₂OH
→
OH
CH₂—
OH
CH₂OH
+ H₂O

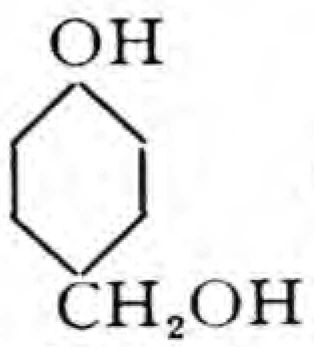
---

[9] Baekeland: U. S. Patents 942,699 and 942,809 (1909).

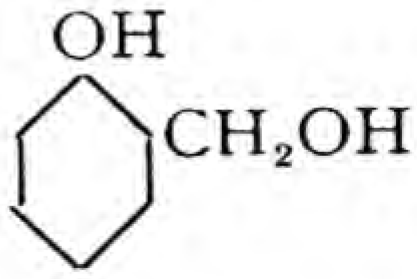
[10] Ellis: *Ind. Eng. Chem.*, **28**, 1130 (1936).

[11] Zinke, Hanus, and Ziegler: *J. prakt. Chem.*, **152**, 126 (1939).

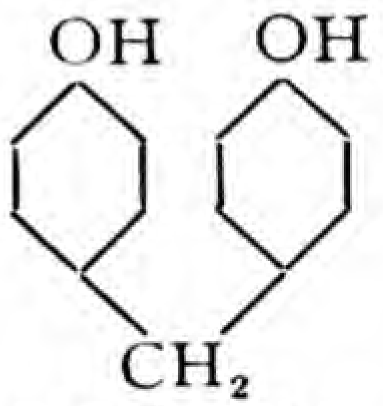
Actually, the course of the reaction depends on the catalyst.[13] If an alkaline catalyst is used, two isomeric hydroxy-alcohols (saligenins) are first formed:

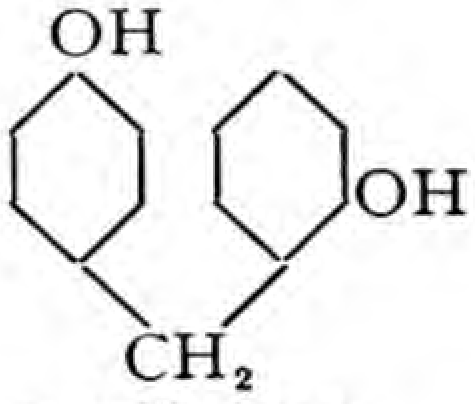

p-hydroxybenzyl alcohol

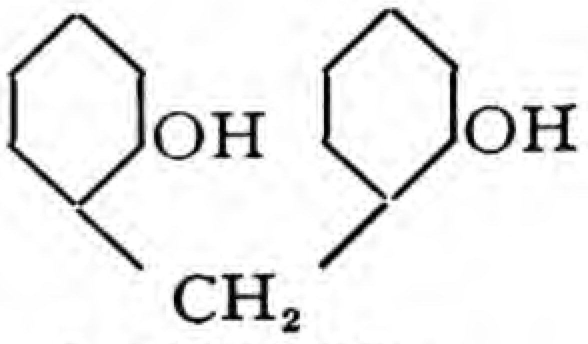
and


o-hydroxybenzyl alcohol

If an acid catalyst is used three dihydroxy-diphenyl methanes are possible:


p-, p-dihydroxy-diphenyl methane


o-, p-dihydroxy-diphenyl methane


o-, o-dihydroxy-diphenyl methane

Baekeland and Bender [14] pictured that the resin formation from phenol and formaldehyde took place as follows:

"(a) Condensation takes place between the hydroxyl hydrogen of the phenol, and the oxygen of the aldehyde or ketone.

(b) The resulting phenoxy group rearranges to a parahydroxy compound.

(c) Condensation takes place between the resulting alcohol and the hydroxyl hydrogen of another phenol molecule.

(d) This mixed phenoxy-phenol compound sometimes rearranges to a diphenol.

(e) The rearrangement in (d) is immaterial to the success or failure of the resinoid reaction."

The actual condensation was calculated to proceed according to the following scheme: [14]

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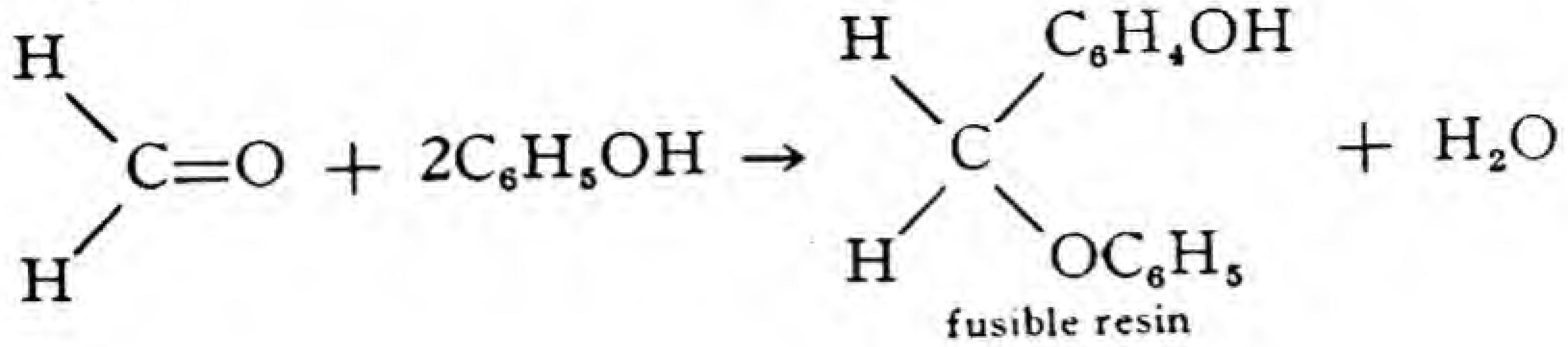
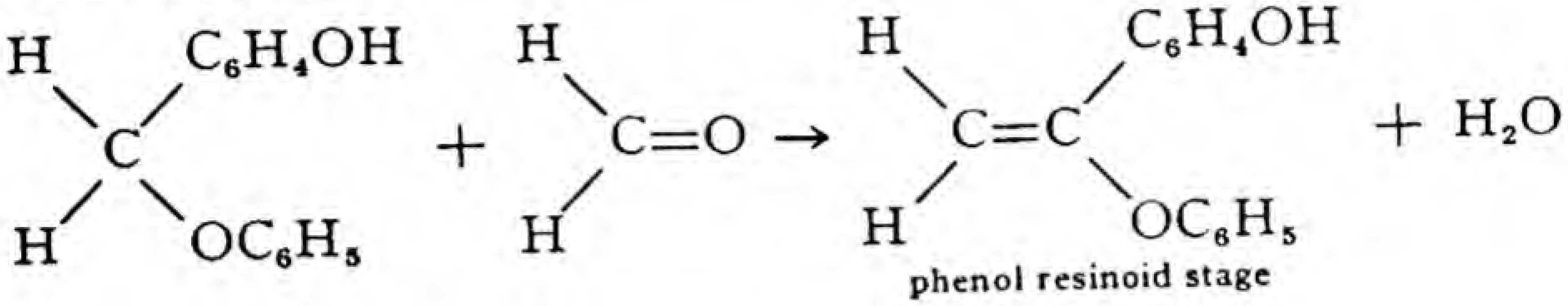
[13] Norton, A. J.: Polymerization, Chapter XIII in Groggins' *Unit Processes in Organic Synthesis*, New York, McGraw-Hill Book Co., Inc., 1938, p. 692.

[14] Baekeland and Bender: *Ind. Eng. Chem.*, **17**, 225 (1925).

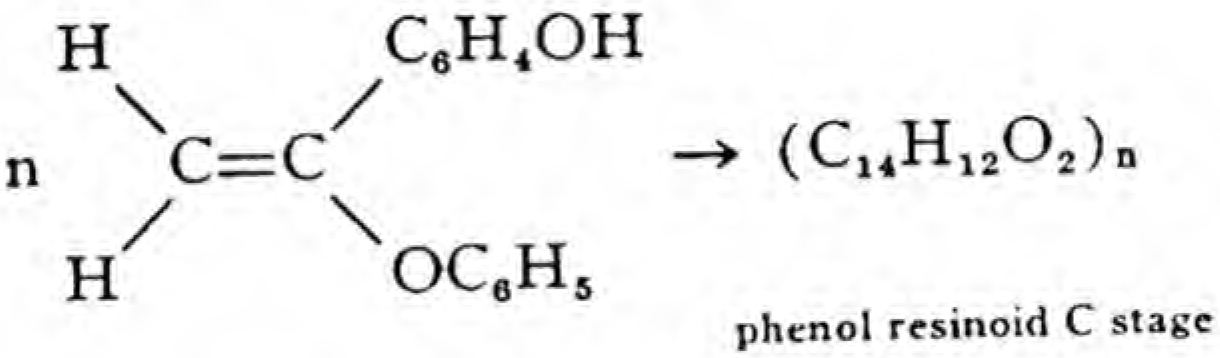
First stage:


fusible resin

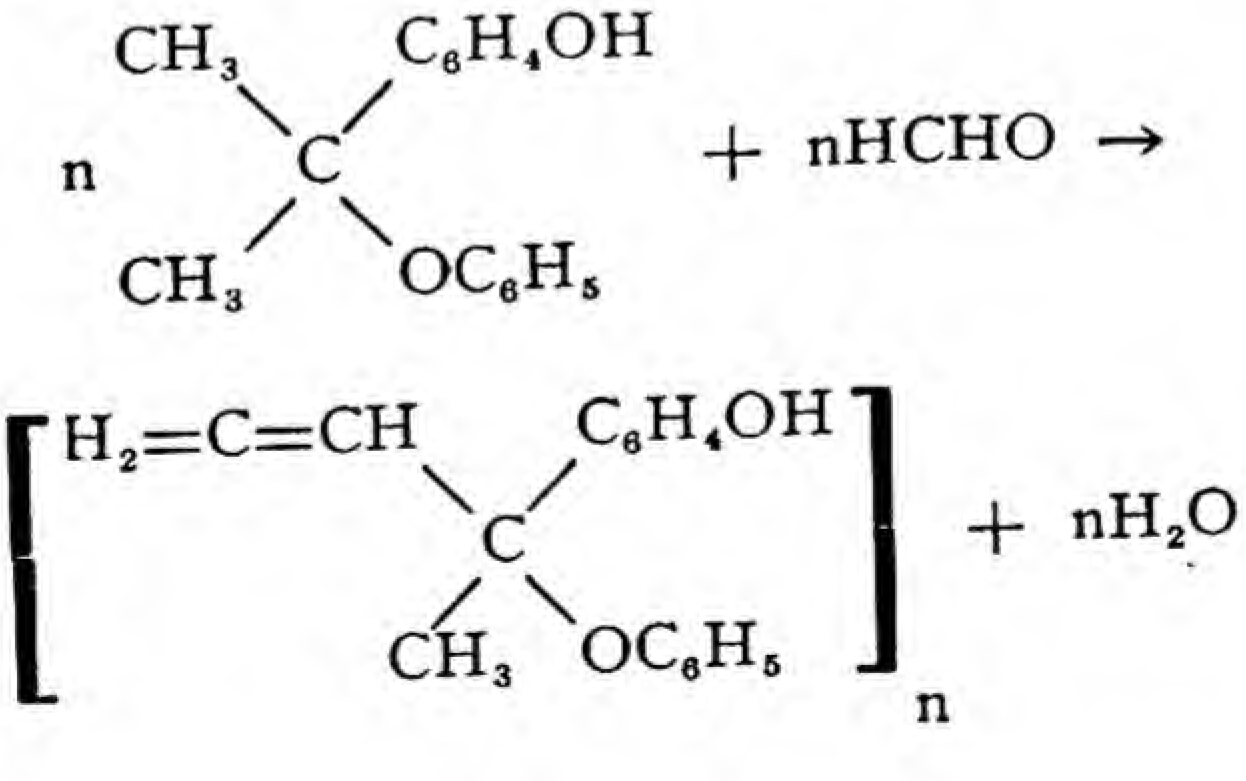
Second stage:


phenol resinoid stage

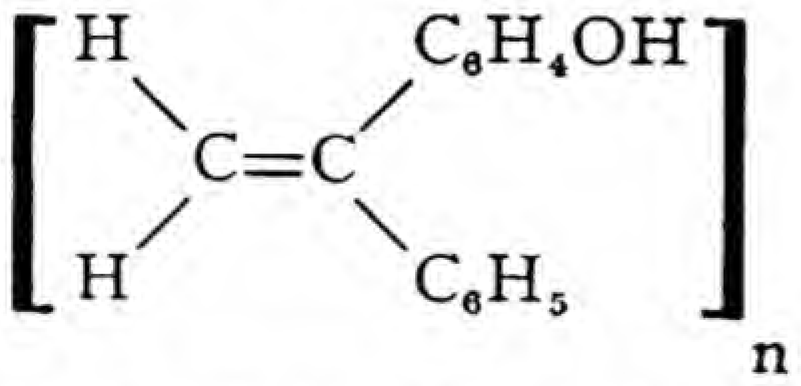
Third stage:


phenol resinoid C stage

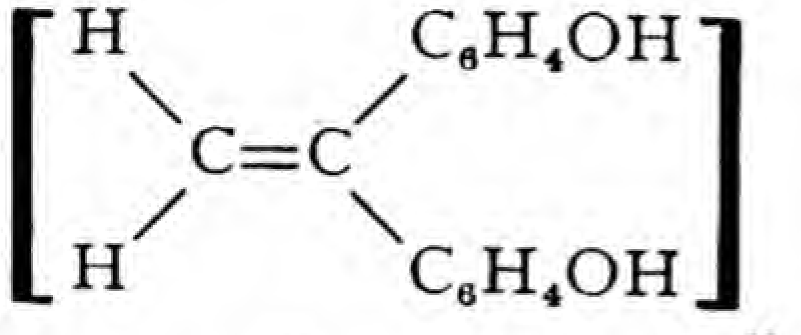
The phenol resinoid B type was considered to be probably a mixture of the A and C types. In the case that ketones or higher aldehydes are used, the result will be a homolog of the above, e.g., using acetone, the following reaction may be obtained:



Those commercial phenol resinoids which are made from phenol and formaldehyde will then consist mainly of the compound:



which will be found in all stages from the initial or uncondensed molecule to the completely condensed form, together with a small amount of



There are also present small amounts of unused phenol, unused hardening agent, generally hexamethylene tetramine, and traces of the various intermediate compounds which are essential in the production of resinoids. It should be mentioned that the phenol-formaldehyde condensation does not require the presence of catalysts.

More recent researches by Megson et al.[15] indicate that cross linkages between the chains are required for the formation of the final insoluble and infusible resins. In studying the reactions of various phenols and cresols with formaldehyde, it appears that resins are formed the more easily the larger is the number of possible isomers. When aldehydes of higher molecular weight than formaldehyde are used in the condensation with phenol, the setting is slower, and the resulting resin is of lower mechanical strength.[13, 16] An exception to this are furfural resins (Buchan).

Alkyd resins (glyptals) are the result of interaction (esterification) of polyacids (e.g., oxalic, maleic, fumaric, citric, phthalic, etc.) with polyhydroxy alcohols (glycol, glycerol, etc.). The usual reaction products are of high molecular weight and resinous nature.[17, 18]

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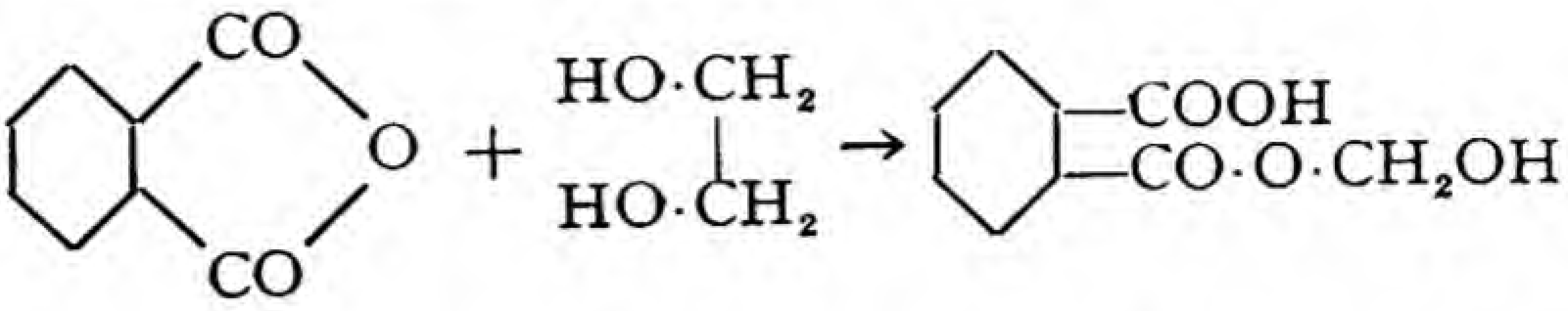
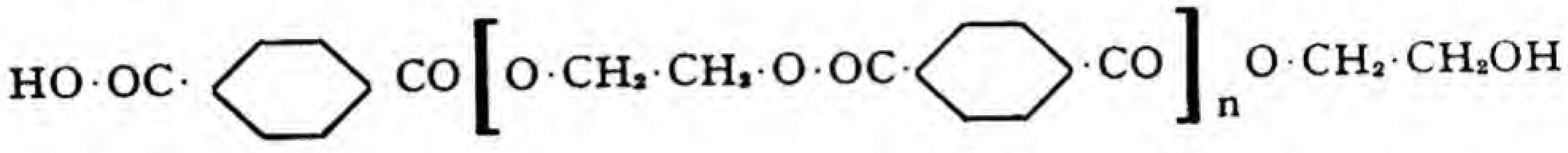
[15] Megson et al.: *J. Soc. Chem. Ind.*, **49,** 251 (1930); *ibid.*, **52T,** 415, 418, 420 (1933).

[16] Trickey, Miner and Brownlee: *Ind. Eng. Chem.*, **15,** 65 (1923).

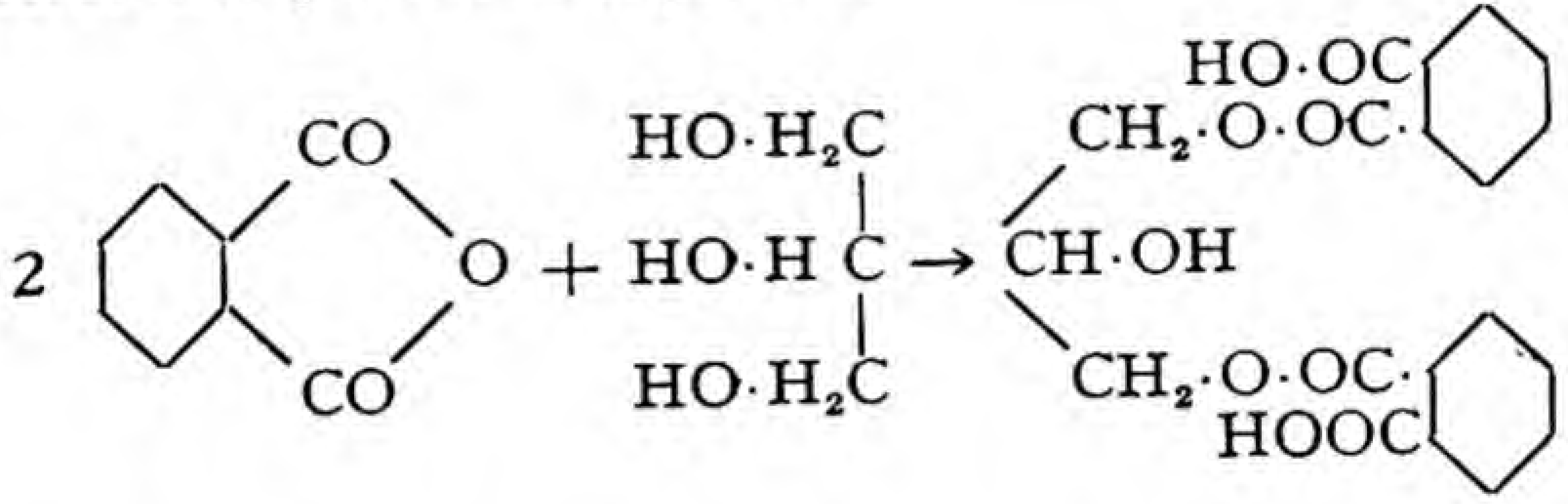
Glycol and phthalic anhydride:



Further addition is possible at the carboxyl group and probably a long-chain molecule is formed:



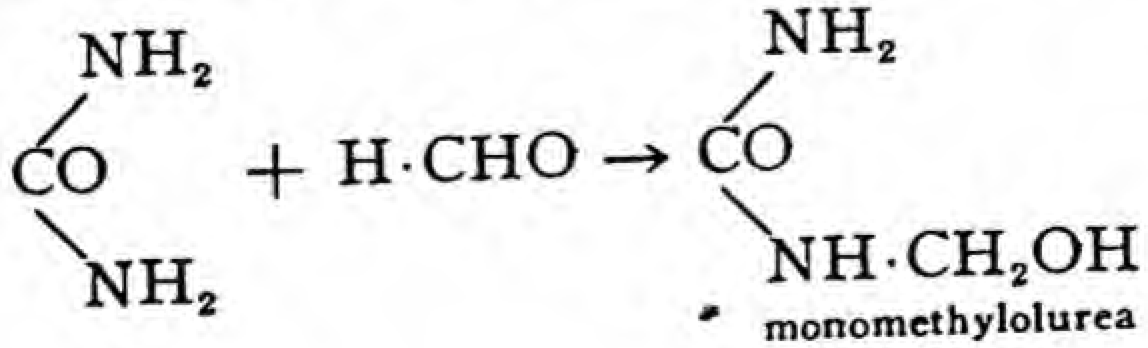
Glycerol and phthalic anhydride:



Further additions of phthalic anhydride and glycerol leads to formation of long chains. The secondary alcohol group reacts with phthalic acid and forms bridges between the chains.[13]

Alkyd or glyptal resins are especially important in the paint and varnish industry.

Urea and formaldehyde condense in aqueous solutions:[19]



monomethylolurea

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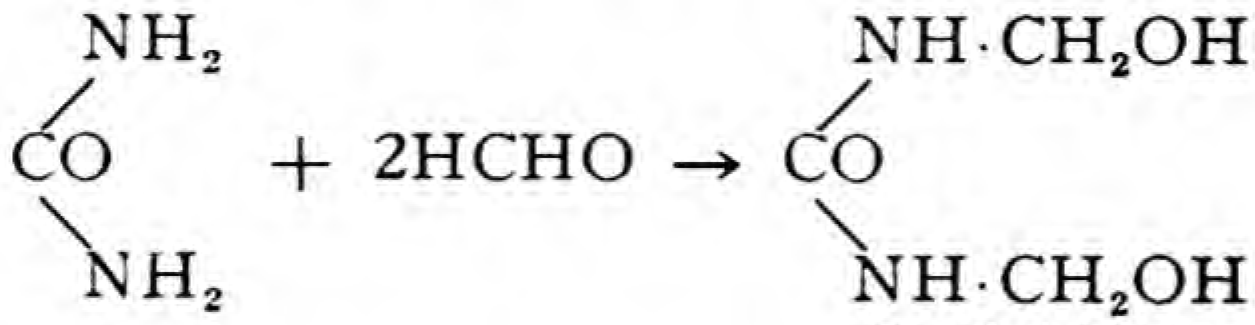
[17] Kienle and Hovey: *J. Am. Chem. Soc.*, **51**, 509 (1929); *ibid.*, **52**, 363 (1930).

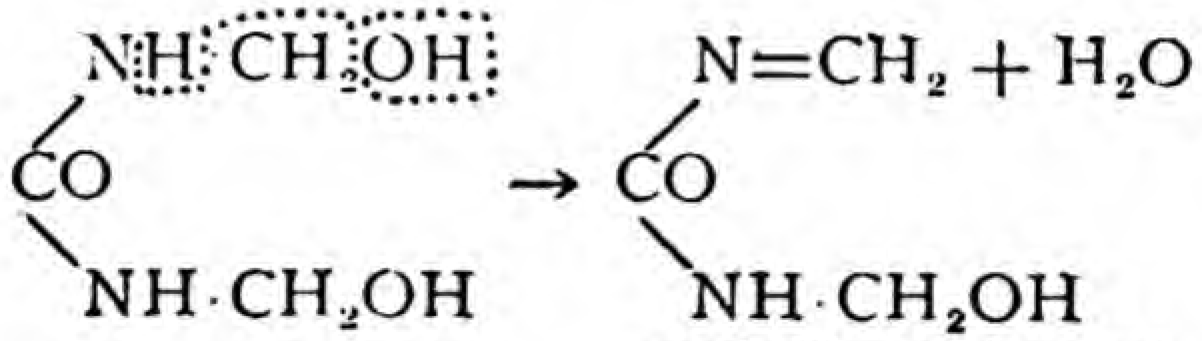
[18] Kienle and Schlingman: *Ind. Eng. Chem.*, **25**, 971 (1933).

[19] Walter: *Trans. Faraday Soc.*, **32**, 377 (1935).

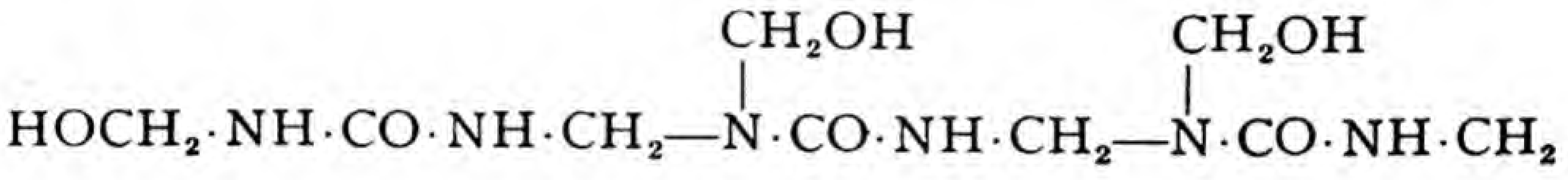


dimethylolurea

Dimethylolurea yields methylol methyleneurea, from which straight-chain polymers are formed, these chains condensing with bridge formation:

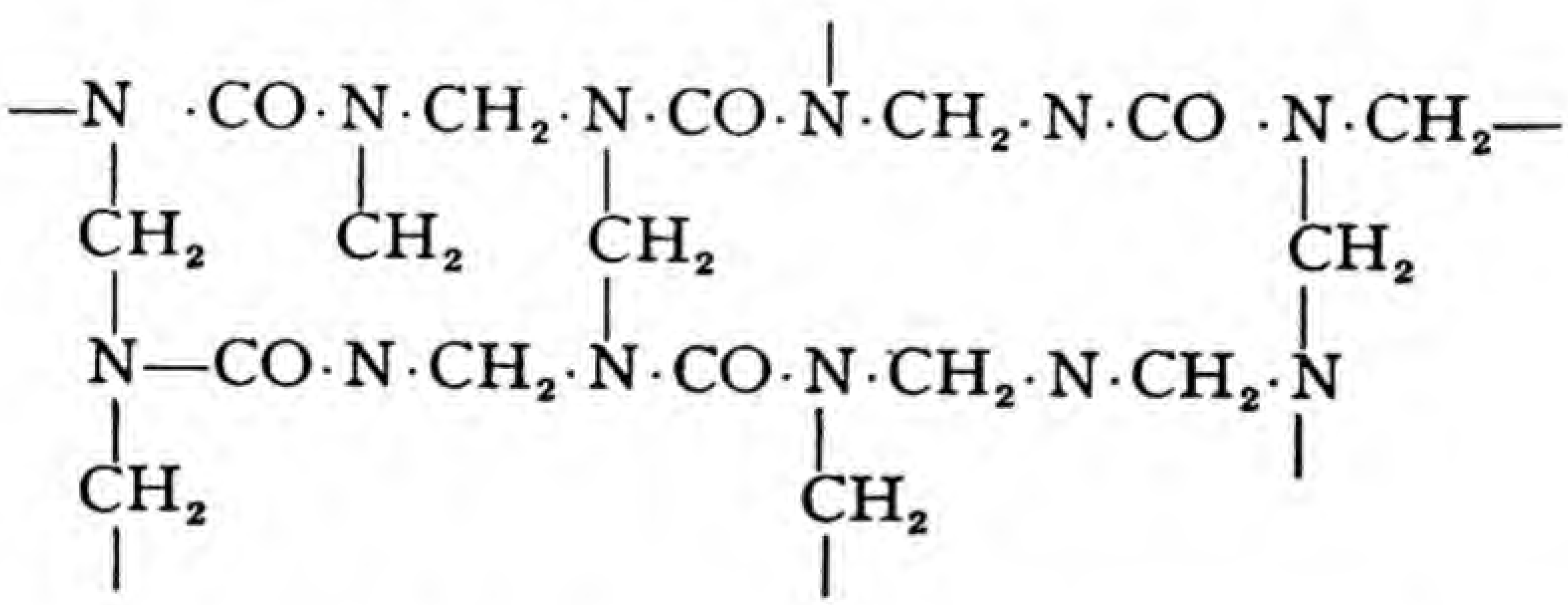


methylol methyleneurea



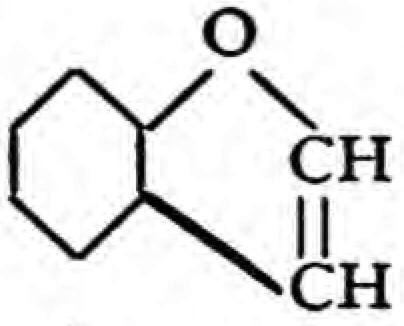
$$\mathrm{HOCH_2\cdot NH\cdot CO\cdot NH\cdot CH_2{-}\overset{\displaystyle CH_2OH}{\overset{|}{N}}\cdot CO\cdot NH\cdot CH_2{-}\overset{\displaystyle CH_2OH}{\overset{|}{N}}\cdot CO\cdot NH\cdot CH_2}$$

which condenses with bridge formation:

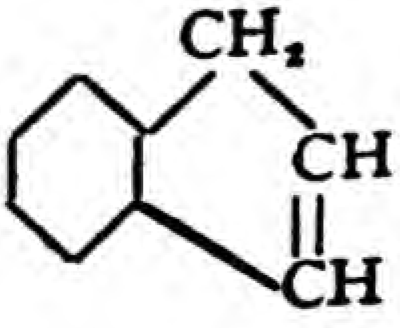


It is supposed that this condensation is more complicated than indicated here. This reaction is considerably influenced by temperature, acidity, and catalytic agents.[19]

Coumarone,



and indene,



combine in the presence of sulfuric acid as a catalyst at 20°C or less to form resins.[20, 21]

13. Polymerization

All polymerization processes are, by no means, catalytic, but a great number of these are, and for this reason, and considering the immense industrial importance of polymerization reactions, some of the more important reaction mechanisms, encountered in polymerization, are discussed briefly.

A polymerized molecule consists of molecular units held together by primary valences.[1, 2, 3, 3a] The reaction involved in building up the polymerized molecule is a chain reaction which progresses by successive additions of monomers to the growing polymer molecule. The length of the chain is considered to be determined by a steric factor. A large steric factor causes the chains to be short. Frequently, the polymerization reaction approximates an autocatalytic path, and an induction period is often observed and is perhaps an essential feature of polymerization reactions.[4]

Classification of high-molecular compounds

Staudinger [1] classifies the organic compounds in low-molecular and high-molecular groups, to the former belong those compounds which can be separated in molecular pure form, and to the latter those which can be separated in pure form, but which consist of homologous macromolecules of average composition. Staudinger's classification is as follows: [1]

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[20] Staudinger, Ashdown, Brunner, Bruson, and Wehrli: *Helv. Chim. Acta*, **12**, 934 (1929).

[21] Whitby and Katz: *J. Am. Chem. Soc.*, **50**, 1163 (1928).

[1] Staudinger, H.: *Die hochmolekularen organischen Verbindungen—Kautschuk und Cellulose*, Berlin, Julius Springer, 1932.

[2] Whitby and Katz: *J. Am. Chem. Soc.*, **50**, 1160 (1928).

[3] Norton, A. J., and E. Emmett Reid: Polymerization, Chapter XIII in Groggins' *Unit Processes in Organic Synthesis*, New York, McGraw-Hill Book Co., Inc., 1938, p. 692.

[3a] Burk: *Ind. Eng. Chem.* **30**, 1054 (1938).

[4] Gee and Rideal: *Trans. Faraday Soc.*, **31**, 969 (1935).

Substance	Molecular weight	Number of carbon atoms in the molecule
Methane	16	1
Low-molecular organic compounds	16–5000	1–500
Polymer or stoichiometric homologous substances:		
Hemi-colloids	1000–10000	100–1000
Eu-colloids	10^4–10^6	10^3–10^{x-1}
High-molecular insoluble substances	10^4–10^x	10^3–10^{x-1}
Diamond, 1 gram—med.	6.06×10^{23}	5×10^{22}

The fractionation of high-molecular homologs becomes increasingly difficult with increasing molecular weight because of the fact that the percentage difference decreases[1] with increasing molecular weight.

The Separation probability in the homologous series of paraffins[1]

$\frac{CH_4}{C_2H_6}$	$\frac{C_2H_6}{C_3H_8}$	$\frac{C_3H_8}{C_4H_{10}}$	$\frac{C_4H_{10}}{C_5H_{12}}$	$\frac{C_5H_{12}}{C_6H_{14}}$	$\frac{C_{10}H_{22}}{C_{11}H_{24}}$	$\frac{C_{50}H_{102}}{C_{51}H_{104}}$	$\frac{C_{100}H_{202}}{C_{101}H_{204}}$
87.5%	47%	32%	24%	19.5%	9.8%	2.0%	1.0%

Due to the impossibility of fractionation of the homologs of high-molecular weight substances, these molecules are characterized by an average molecular weight only.

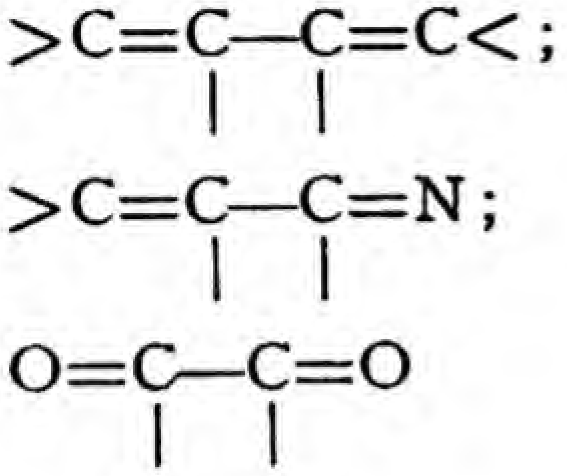
Considering the immense importance of high-molecular compounds in the living organism and the fact that the single molecule species does not lend itself to isolation, or at least not readily so, it may be concluded that much vital knowledge is still obscure in colloid chemistry and biology. The progressing knowledge of biocatalysts, vitamins and hormones also points toward this conclusion(Lohse).

The influence of various linkages and other structural characteristics has been discussed by various authors.

Unsaturation is necessary for true polymerization, a matter which has been well illustrated among others by Staudinger,[1] Norton and Reid.[3] The latter present the following classification:

1. $-C\equiv C-$; $>C=C<$; $-C\equiv N$; $>C=N-$; $>C=O$ — Unsaturation on two atoms

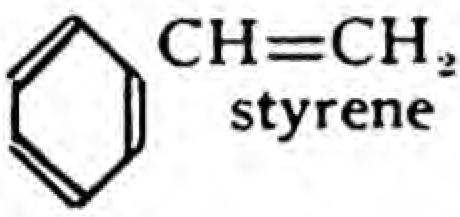
2. $>C=\overset{*}{C}=$; $>C=\overset{*}{C}=O$; $>C=\overset{*}{C}=N=$ — Unsaturation on one atom (*)—Polymerization tendency > group (1)

3. 

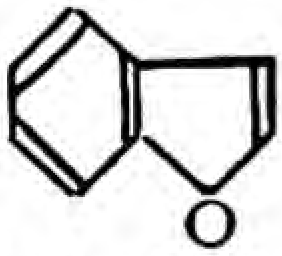
$$>C=\underset{|}{C}-\underset{|}{C}=C<;\quad >C=\underset{|}{C}-\underset{|}{C}=N;\quad O=\underset{|}{C}-\underset{|}{C}=O$$

Conjugated unsaturation — Polymerization tendency > group (2)

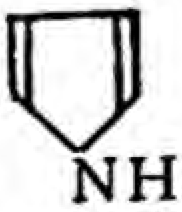
4\.

	negative group	
 styrene	phenyl	Negative groups attached to a vinyl radical tend to form highly polymerized polymers
$CH_2=CH\cdot COOH$ acrylic acid	carboxyl	
$CH_2=CH\cdot CHO$ acrolein	aldehyde	
$CH_2=CH\cdot COCH_3$ methylene acetone	acetyl	
$CH_2=CH\cdot OCOCH_3$ vinyl acetate	acetoxy	
$CH_2=CH\cdot OCH_2CH_3$ vinyl ethyl ether	ethoxy	
$CH_2=CH\cdot Cl$ vinyl chloride	chloride	

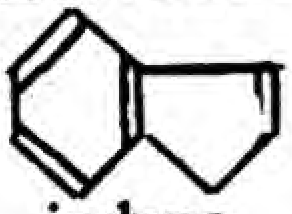
5\.



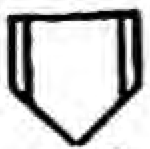
coumarone



pyrole



indene



cyclopentadiene

Polymerization possible, but giant molecules not formed

Staudinger[5] classifies the polymerization tendency of ethylene and carbonyl derivatives as follows:

Compound C=C	Polymerizes	Compound C=O	Polymerizes
$CH_2{=}CH_2$	with some difficulty	$CH_2{=}O$	very easily
$CH_3{\cdot}CH{=}CH_2$	with difficulty	$CH_3CH{=}O$	easily
$(CH_3)_2C{=}CH_2$	easily	$(CH_3)_2C{=}O$	condenses only
$CH_2{=}CH{-}CH{=}CH_2$	easily	$CH_2{=}CH{\cdot}CH{=}O$	very easily
$C_6H_5{=}CH{=}CH_2$	very easily	$C_6H_5{\cdot}CH{=}O$	condenses only
$CH_3O{\cdot}CO{\cdot}CH{=}CH_2$	very easily	$CH_3O{\cdot}CO{\cdot}CH{=}O$	very easily
$CH_3CO{\cdot}CH{=}CH_2$	very easily	$CH_3CO{\cdot}CH{=}O$	easily
$CH_3CO{\cdot}OCH{=}CH_2$	easily	$CH_3O{\cdot}CH{=}O$	no polymerization
$Cl_2C{=}CH_2$	easily	$Cl_2C{=}O$	no polymerization
$O{=}C{=}CH_2$	easily	$O{=}C{=}O$	no polymerization

The polymerization reaction is accelerated by rise in temperature, and, as a rule, temperature increases the tendency to polymerization, although there are exceptions such as cyclopentadiene the polymerization tendency of which is increased by heating.[3, 4, 5, 5a] Slow polymerization, usually, yields the largest molecules.[3a] Pressure, generally, decreases the polymerization tendency. It is well known that radiations (light) also influence the polymerization, the influence being specific for different reactions. When styrene is polymerized in a solvent, the resulting polymer has a lower molecular weight than the product prepared in the absence of the solvent.

Polymerization catalysts are numerous and, in many cases, specific in their action.[3a, 5a, 6] The mineral acids, BF_3 with or without hydrogen halide, $AlCl_3$ with Zn, $ZnCl_2$, noble metals, silica gel, acids, metals of the eighth series, oxides, activated clays, bauxite, alkalies, salts, organic peroxides, nitrogen bases, catalytically prepared metals, and for that matter many other compounds serve as catalytic agents in polymerization.[1, 2, 3a, 6] Attention is also called to the use of hydrogen peroxide as a polymerizing agent.[6] In the presence of HF, natural and synthetic resins become hard and brittle. Unsaturated compounds, containing olefin linkage (olefins, vegetable oils), are also polymerized by this agent.[9]

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[5] Staudinger: *Trans. Faraday Soc.*, **32**, 97 (1936).

[5a] Staudinger et al.: *Helv. Chim. Acta*, **12**, 934 (1929).

[6] R. E. Burk, H. E. Thompson, A. J. Weith, and J. Williams: *Polymerization and Its Application in the Fields of Rubber, Synthetic Resins, and Petroleum*, New York, Reinhold Publishing Corp., 1937; R. E. Burk: *Catalysis in Polymerization*, Twelfth Report of the Committee on Catalysis, National Research Council, New York, John Wiley & Sons, Inc., 1940, p. 180.

Burk [3a] has summarized the frequency with which the different polymerization catalysts are used in published papers and patents up to and inclusive 1936, some of his data being as follows:

Metals		233
Alkali metals	68	
Alkaline earth metals	24	
Copper	19	
Iron	17	
Nickel	18	
Acids		231
Acids (general)	58	
Acetic acid	11	
Acids of phosphorus	37	
Sulfuric acid	71	
Halides		219
Aluminum halides	77	
Zinc halides	35	
Boron halides	41	
Tin halides	21	
Oxidizing agents		132
Peroxides	75	
Oxygen	28	
Oxidizing agents (general)	15	
Oxides		63
Silica	14	
Alumina	10	
Copper oxides	6	
Clays		35
Nitrogen bases		34
Hydroxides (alkali)		31
Carbon		26
Alkalies (see also hydroxides)		25
Organometallic compounds		11
Hydroxides (alkaline earths)		8

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[9] Simons: *Ind. Eng. Chem.*, **32**, 178 (1940).

Soaps	7
Other classifications (less than five examples of each)	90
Total	1154

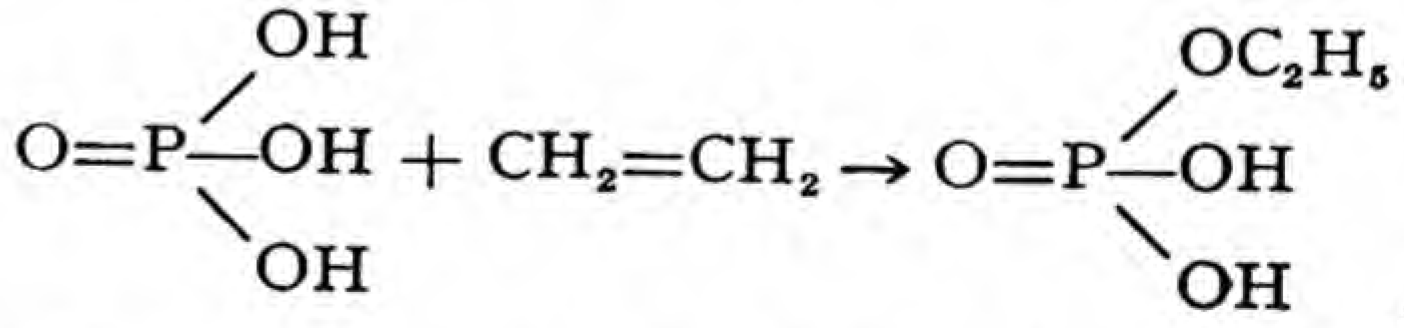
These data are entirely statistic and should be judged as such. An important catalyst may occur with low frequency, and vice versa.

The polymerization of olefins by acids is, by now, a very important process in the gasoline industry.[10] The kinetics of polymerization has been discussed by Semenov,[11] Ginell and Simla,[12] Schulz,[13] Gwyn Williams,[14] and others.

Polymerization of ethylene was studied by Ipatieff [15, 15a] who polymerized this gas at 330°C and under superatmospheric pressure (50 kg/m^2), using phosphoric acid as catalyst. From this resulted a mixture of hydrocarbons, consisting of paraffins, olefins, naphthenes and aromatics.

The mechanism of this experiment is suggested to be as follows:

(1) The first reaction is the formation of ethyl phosphates:



$$\mathrm{O{=}P}\begin{array}{l}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array} + \mathrm{CH_2{=}CH_2} \rightarrow \mathrm{O{=}P}\begin{array}{l}\diagup\mathrm{OC_2H_5}\\ -\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array} \qquad \mathrm{(I)}$$

(2) As the ethyl phosphates are unstable at higher temperatures, they decompose to yield polymers and naphthenes:

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[10] McAllister, S. H.: *The Catalytic Polymerization of Butylene by Sulfuric Acid*, 8th Annual Meeting, Am. Petroleum Inst., November, 1937.

[11] Semenov, N.: *Chemical Kinetics and Chain Reactions*, Oxford, The Clarendon Press, 1935.

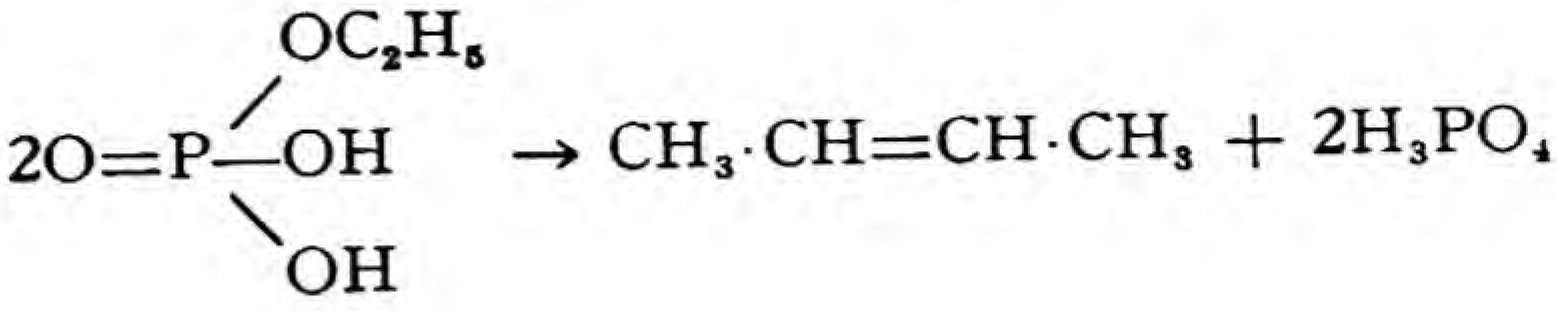
[12] Ginell and Simla: *J. Am. Chem. Soc.*, **65**, 706, 715 (1943).

[13] Schulz, G. V.: *Kinetik der Polymerizationsprozesse*, Ergeb. exakten Naturw., Berlin, Julius Springer, 1938.

[14] Gwyn Williams: *J. Chem. Soc.*, 775 (1940).

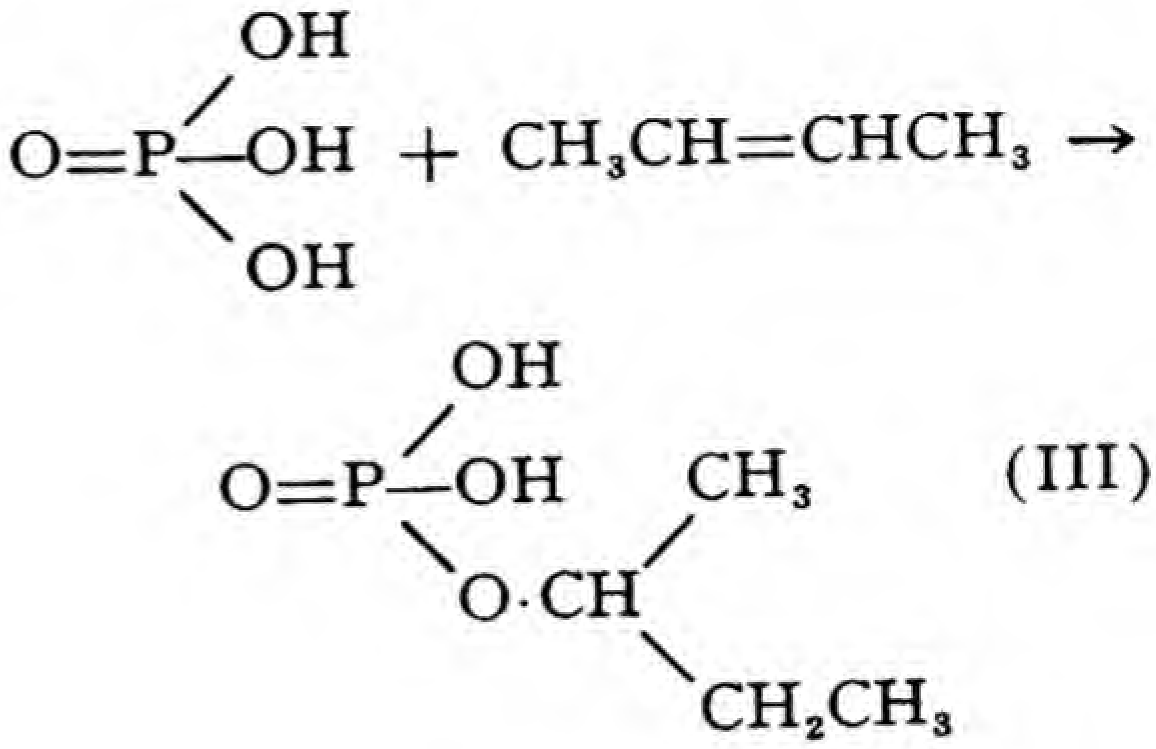
[15] Ipatieff and Pines: *Ind. Eng. Chem.*, **27**, 1364 (1935).

[15a] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures*, The Macmillan Co., New York, 1937.



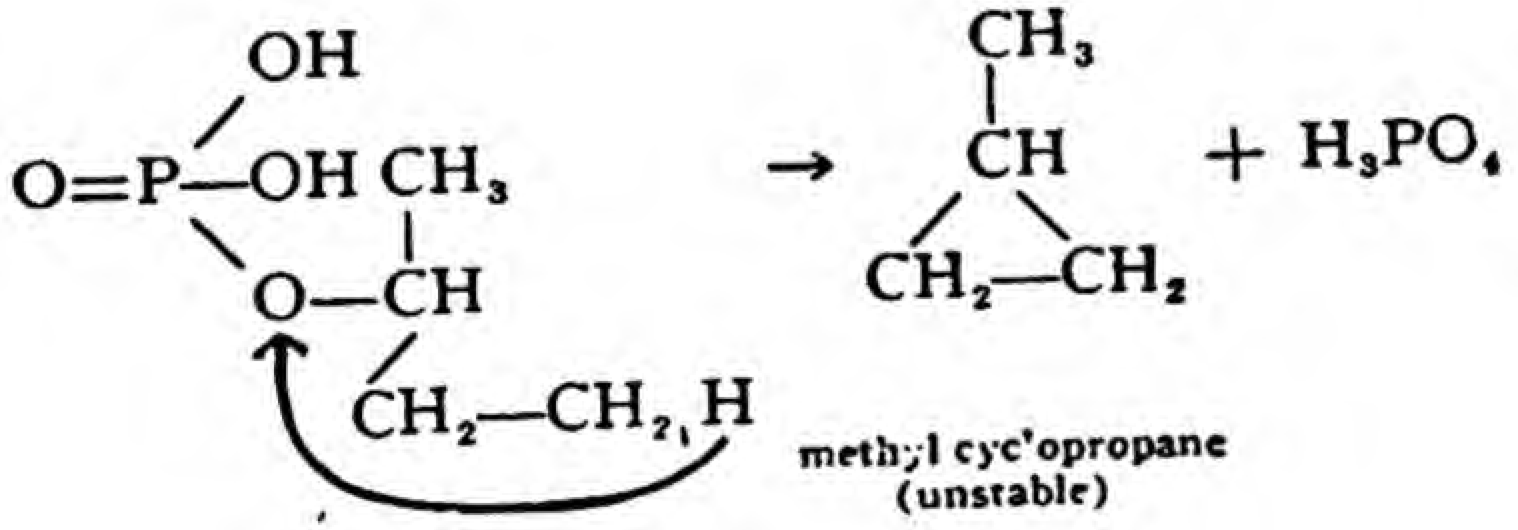
$$2O{=}P(OC_2H_5)(OH)(OH) \rightarrow CH_3\cdot CH{=}CH\cdot CH_3 + 2H_3PO_4$$

(II)

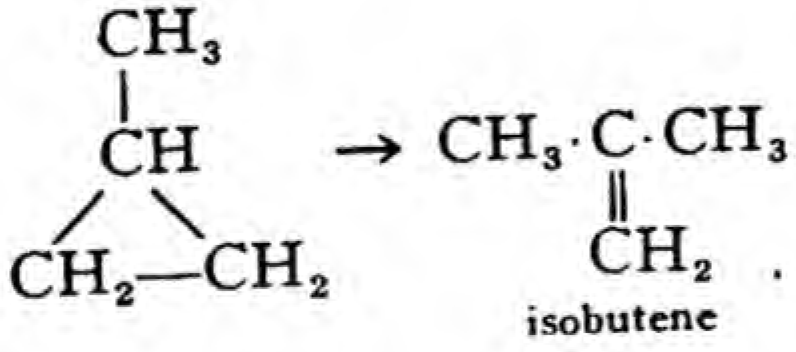


$$O{=}P(OH)(OH)(OH) + CH_3CH{=}CHCH_3 \rightarrow O{=}P(OH)(OH)(O\cdot CH(CH_3)(CH_2CH_3))$$

(III)



(IV)



(3) Naphthenic hydrocarbons dehydrogenate to form aromatic hydrocarbons.

(4) Olefin hydrocarbons are hydrogenated to paraffins with hydrogen derived from the dehydrogenation of naphthenes to aromatics, reactions (3) and (4) taking place simultaneously, and the hydrogenation being exerted by the hydrogen in its nascent state.

(5) Besides these reactions, the following may also occur:

   I. Alkylation of aromatic hydrocarbons with ethylene resulting in formation of ethyl benzenes.
   II. Partial dehydrogenation of naphthenes to yield polycyclic naphthenes.
   III. Isomerization of olefinic hydrocarbons.

As polymerization is understood to represent a reaction in which a molecule combines with other molecules of the same kind to form a larger molecule which is a multiple of the original, the process of treating ethylene at high temperature and pressure, which yields different products, is not a true polymerization process. Ipatieff calls such a process conjunct polymerization.

Farkas and Farkas [16] arrived at a modified mechanism by studying the polymerization of isobutene and other olefins on a phosphoric acid catalyst in which the hydrogen atoms were replaced by deuterium atoms (D_3PO_4).

Wachter [17] gave the following rule: "In the polymerization of lower olefins, the least substituted double-bonded carbon detaches a hydrogen atom, and the resulting bond adds to the most substituted double-bonded carbon of the second molecule."

A brief summary of a technical polymerization process * utilizing the lower olefins, dealing with the C_4 fraction of a feed stock, containing 18.5 per cent isobutylene and 28 per cent normal butylenes, deserves mention.[10]

The isobutylene is selectively absorbed by contacting countercurrently in two stages with 60 to 70 per cent H_2SO_4 at 20–35°C, about 90 per cent of the isobutylene being absorbed whereas no appreciable absorption of the normal butylenes occurs. The isobutylene—H_2SO_4 fraction is heated to 100°C, and the polymerization reaction is finished in one minute. The polymer and the acid are separated, the acid being used over again and the polymer washed and distilled.

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[16] Farkas and Farkas: *Ind. Eng. Chem.*, **34**, 716 (1942).
[17] Wachter: *Ibid.*, 30, 822 (1938).
* Compare with alkylation process by Dunstan and Birch (pages 259, 260).

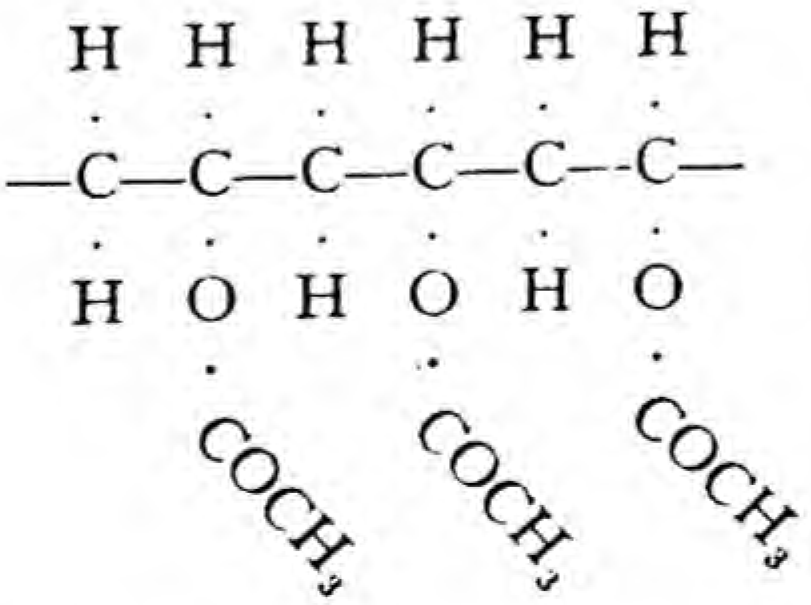
A 65 per cent acid yields a polymer consisting of about 75 per cent di-isobutylene, the balance being trimers. From mild hydrogenation of the di-isobutylene cut, iso-octane (2,2,4-trimethyl pentane) results. By using hot acid (80°C), almost twice the yield of octanes is obtained from the same feed stock. Above 60°C, the polymerization is sufficiently rapid that the absorbed isobutylene has only a transitory life in the acid phase.

Specifically for the processes reported by McAllister,[10] the comparative efficiency of cold-acid and hot-acid operation is as follows:

	65% Acid 30–35° C	65% Acid 80° C	65% Acid 90° C
Fuel composition: (% by weight)			
Isobutylene	18.5	18.5	9.1
n-Butylene	28.0	28.0	20.6
Butanes	53.5	53.5	70.3
Products: (%)			
Isobutylene	2.4	0	0
n-Butylenes	26.6	15.1	11.4
Butanes	53.5	53.5	70.3
Polymer	17.5	31.4	18.3
Isobutylenes polymerized	87	100	100
n-Butanes polymerized	5	46.0	44.5
Total olefins polymerized	37.5	67.5	61.5
Composition of polymer: (%)			
Sulfur (A.S.T.M.)	0.01	0.03*	0.062*
Octenes	75	88	92
Octane rating of hydrogenated octenes	100	99.2	98.8

* Negligible sulfate esters present.

Staudinger[18] assumed that in polyvinyl derivates, many vinyl groups are combined to form an unbranched saturated carbon chain:



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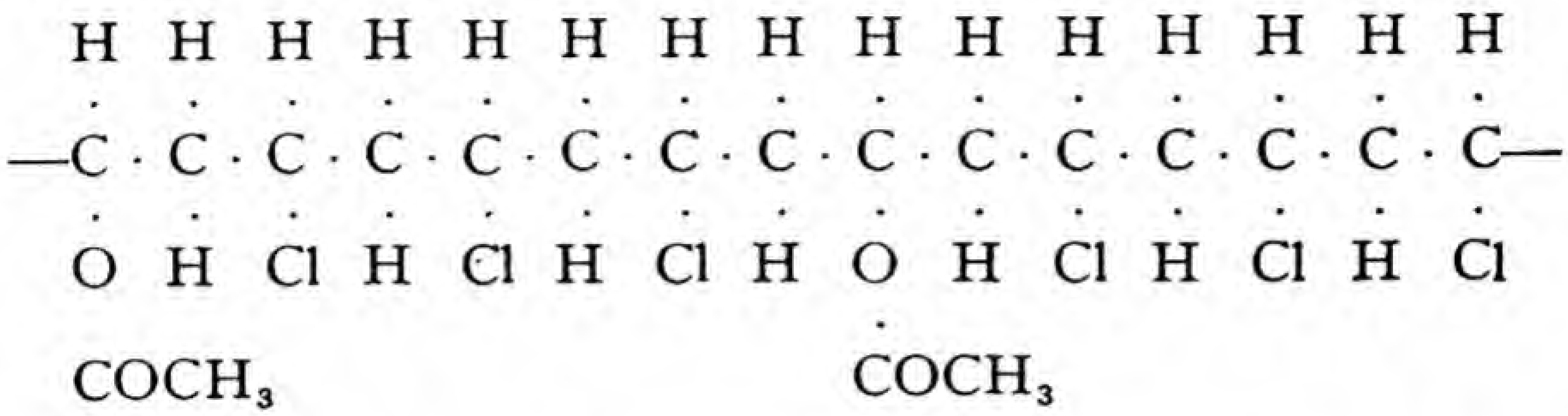
[18] Staudinger: *Ber.*, **60**, 1782 (1927).

This compound reacts as an ester of a saturated polyhydric alcohol.

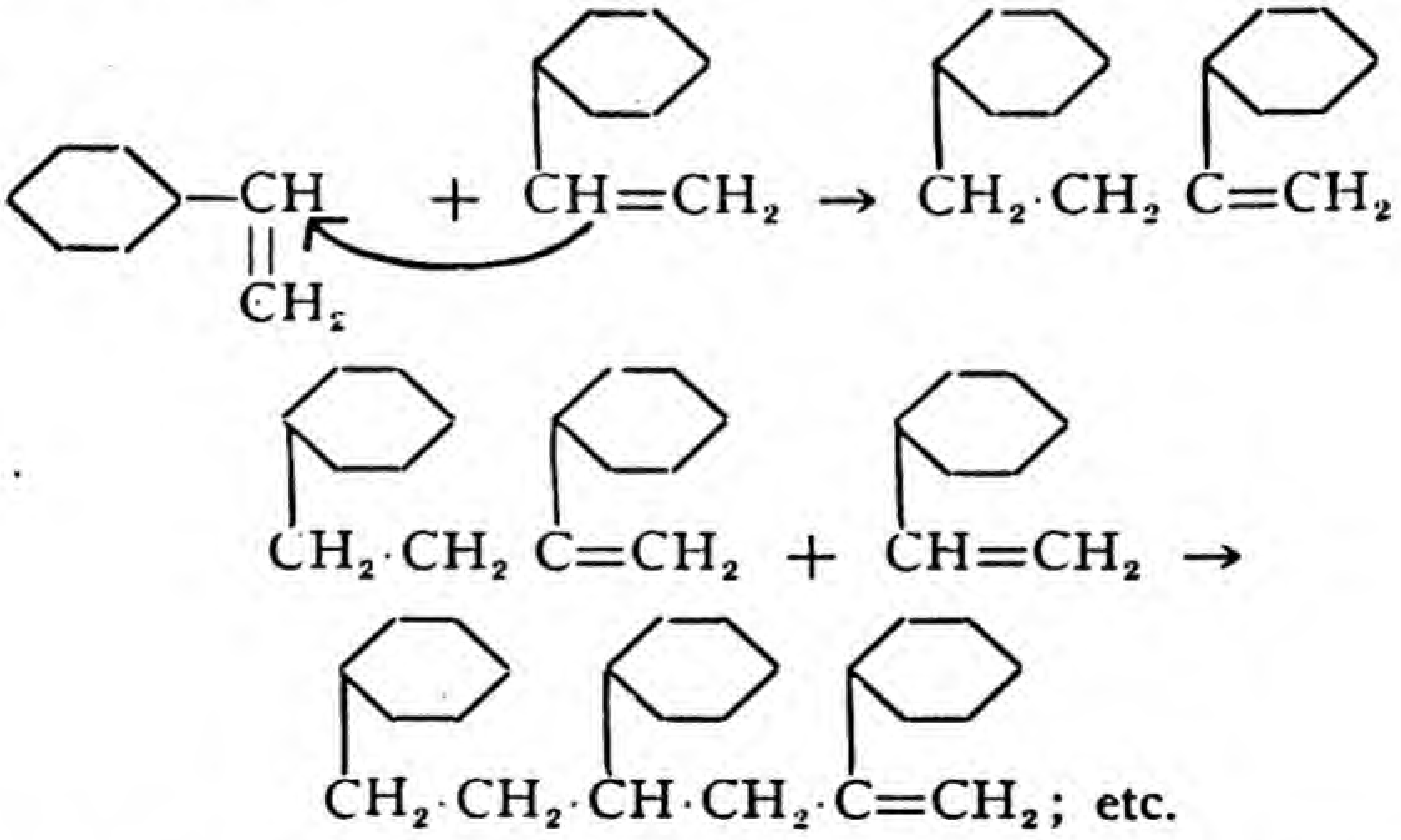
Copolymers (conjoint polymers) are formed from vinyl chloride ($CHCl{=}CH_2$) and vinyl acetate ($CH_2{=}CH{\cdot}O{\cdot}CO{\cdot}CH_3$), the structure of which is considered to be:[19, 20]



$$\begin{array}{ccccccccccccccccc}
 & H & H & H & H & H & H & H & H & H & H & H & H & H & H & H & \\
 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \\
- & C & C & C & C & C & C & C & C & C & C & C & C & C & C & C & - \\
 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \\
 & O & H & Cl & H & Cl & H & Cl & H & O & H & Cl & H & Cl & H & Cl & \\
 & & & & & & & & & \cdot & & & & & & & \\
 & COCH_3 & & & & & & & & COCH_3 & & & & & & &
\end{array}$$

Recent structural studies, as related to polymerization, should also be consulted.[21, 22]

As to styrene, Whitby and Katz,[2] Whitby,[22a] and Staudinger and Lautenschaeger [23] found that the additions take place through the double bond:



The polymerization of styrene is brought about by heat, radiations or adsorption at the surface of a catalyst. Oxygen or air

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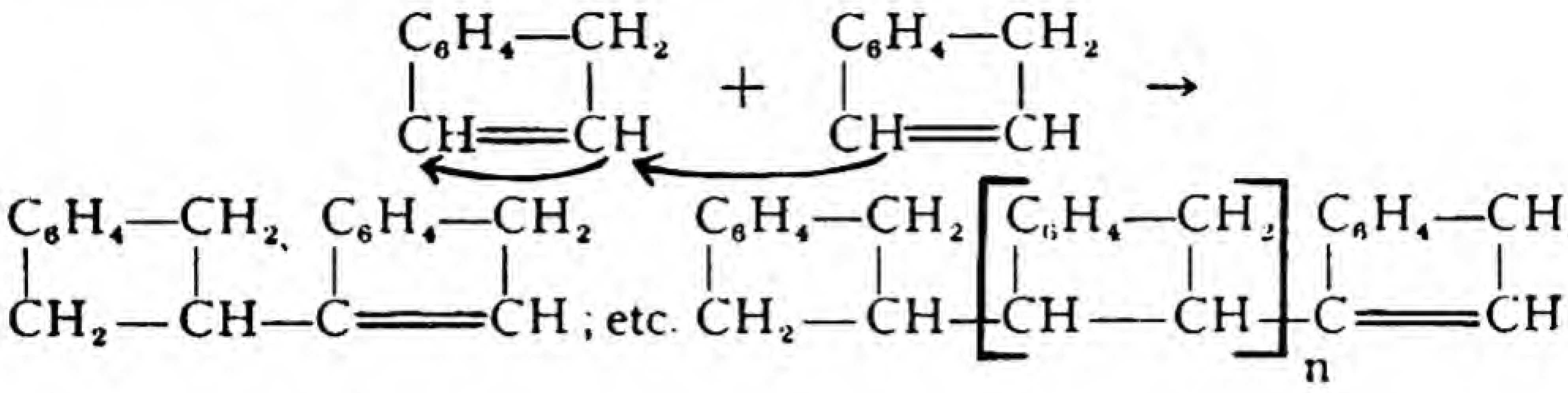
[19] Ellis: *Ind. Eng. Chem.*, **28**, 1136 (1942).
[20] Curme and Douglas: *Ibid.*, **28**, 1126 (1936).
[21] Reinhardt: *Ind. Eng. Chem.*, **35**, 422 (1943).
[22] Baker and Fuller: *J. Am. Chem. Soc.*, **65**, 1120 (1943).
[22a] Whitby: *Trans. Faraday Soc.*, **32**, 315 (1936).
[23] Staudinger and Lautenschlaeger: *Ann.*, **488**, 1 (1931).

accelerate this polymerization. The chains are longer without a catalyst than with a catalyst.

Indene polymerizes similarly:[2]



Chains of polymers, containing 50 to 100 monomeric molecules, dissolve readily to yield solutions of low viscosity unaltered by heat. By addition of a non-solvent the polymer precipitates as an amorphous powder. Polymers, consisting of 3000 monomeric molecules or more, yield (colloidal) solutions of high viscosity. These long chains decompose, at higher temperatures, into shorter ones yielding a solution of lower viscosity.

The following table presents some interesting data on polystyrene polymer homologs:[1, 18]

Polymer	Formula		Molecular weight	Degree of polymerization	Property of polymer	Solubility in ether	Sintering point °C
Dimer	C_{16}	H_{16}	208	2	Fluid	Soluble	—
Trimer	C_{24}	H_{24}	312	3	Fluid	Soluble	—
Hemicolloid (polymerized with SnCl)	C_{240}	H_{240}	3,000	30	White powder	Soluble	105–110
Polymerized at 150° C (in nitrogen atmosphere)	C_{1840}	H_{1840}	23,000	230	White powder	Partly soluble	120–130
Polymerized at 100° C (in nitrogen atmosphere)	C_{9600}	H_{9600}	120,000	1,200	White fiber	Insoluble	160–180
Polymerized at 20° C (in air)	C_{16000}	H_{16000}	200,000	2,000	White fiber	Insoluble	> 180
Polymerized at room temperature (in nitrogen atmosphere)	C_{4800}	H_{48000}	600,000	6,000	White fiber	Insoluble	> 180

Depolymerization is the opposite of polymerization, i.e., the disaggregation of a polymer molecule into monomer molecules. This process is usually endotherm.

A well known reaction is the depolymerization of paraldehyde into three molecules of acetaldehyde:

$$\underset{\text{paraldehyde}}{C_6H_{12}O_3} \rightleftarrows \underset{\text{acetaldehyde}}{3CH_3CHO}$$

This reaction is catalyzed by acids and bases.[24]

Carothers et al.[25] found that six-membered cyclic esters polymerize reversibly, whereas esters which are five-membered or more than six-membered do not polymerize under the influence of heat.

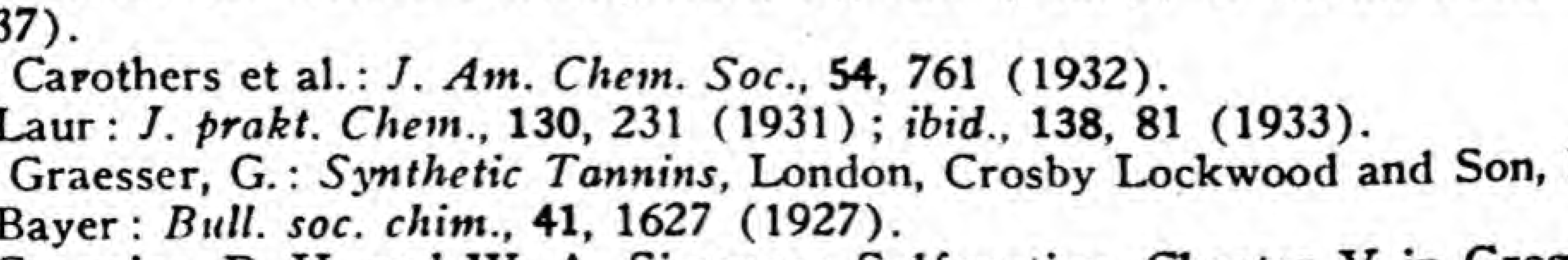
GENERAL REFERENCES

Staudinger and Rheiner: *Helv. Chim. Acta*, **7**, 23 (1924); Kistiakowsky and Mears: *J. Am. Chem. Soc.*, **58**, 1060 (1936); Mayo, F. R.: *Chain transfer in the polymerization of styrene. The reactivities of solvents with free radicals.* Paper read at the spring-meeting of the American Chemical Society, Detroit, April, 1943. (With permission of the author.)

14. Sulfonation

Catalysts are used in sulfonation as accelerators of the reaction as well as agents for forming special compounds. The most common sulfonation catalysts are mercury, mercury salts, vanadium oxide, vanadium salts, boric acid, alkali carbonates,[3] alkali sulfates and phosphorus pentoxide.[1a]

If anthraquinone is sulfonated without a catalyst, β-derivatives are formed, but if about half to one per cent of mercuric sulfate is added to the sulfonation mixture, α-derivatives are formed. A step in this reaction is the formation of an intermediary compound with the mercuric sulfate in the α-position:[1, 2, 3]



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[24] Bell et al.: *Trans. Faraday Soc.*, **33**, 355 (1937); *J. Chem. Soc.*, 1947, (1937).

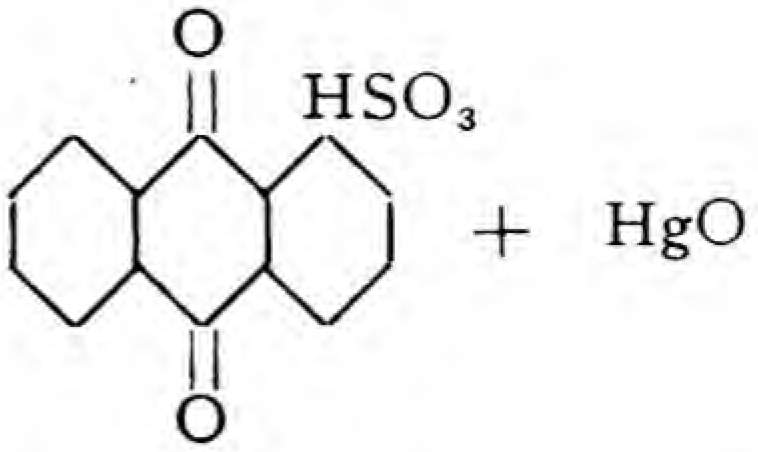
[25] Carothers et al.: *J. Am. Chem. Soc.*, **54**, 761 (1932).

[1] Laur: *J. prakt. Chem.*, **130**, 231 (1931); *ibid.*, **138**, 81 (1933).

[1a] Graesser, G.: *Synthetic Tannins*, London, Crosby Lockwood and Son, 1922.

[2] Bayer: *Bull. soc. chim.*, **41**, 1627 (1927).

[3] Groggins, P. H. and W. A. Simpson: Sulfonation, Chapter V in Groggins' *Unit Processes in Organic Synthesis*, New York, McGraw-Hill Book Co., Inc., 1938, p. 233.



By further sulfonation of the α-monosulfuric acid in the presence of mercury, the 1,5- and 1,8-derivatives are obtained.

If benzoic acid is sulfonated without a catalyst, meta and para derivatives are obtained, but in the presence of mercuric sulfate, the ortho derivative is formed.[4]

If benzene is sulfonated in the presence of aluminum chloride, it forms $C_6H_5 \cdot SO_2H$ or, more likely, $C_6H_5 \cdot SO_2 \cdot AlCl_2$. This reaction is accelerated by HCl.[5, 6]

Whereas chlorination reactions with SO_2Cl_2 occur with many types of organic compounds in the presence of a peroxide catalyst, sulfonation takes place when other catalysts are used, the catalyst, more than any other factor, determining the course of the reaction.[7, 8]

A series of useful chemicals (wetting agents, emulsifiers, solvents) are made by sulfonating high-molecular aliphatic or cycloaliphatic alcohols, or alcohols containing aromatic or hydroaromatic radicals, in the presence of aldehydes.[9] Suitable aldehydes are claimed to be formaldehyde, acetaldehyde, propionaldehyde, and compounds acting as aldehydes such as acetal, aldehyde bisulfite and aldehyde ammonia compounds. As sulfonating agents are used sulfuric acid, fuming sulfuric acid, or $HClSO_3$. Promoters, such as anhydrous acetic acid, $POCl_3$ or P_2O_5, may be used with the sulfonating agent. The sulfonated compounds are soluble in water and in acid and alkaline solutions.

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[4] Dimroth and Schmoedel: *Ber.*, **40**, 2411 (1907).

[5] Friedel and Crafts: *Ann. chim. phys.*, **14**, 443 (1888).

[6] Knoevagel and Kenner: *Ber.*, **41**, 3315 (1908).

[7] Kharasch and Read: *J. Am. Chem. Soc.*, **61**, 3089 (1939).

[8] Kharasch and Brown: *Ibid.*, **62**, 925 (1940).

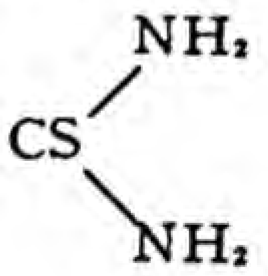
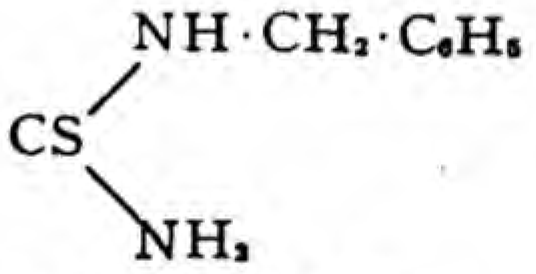
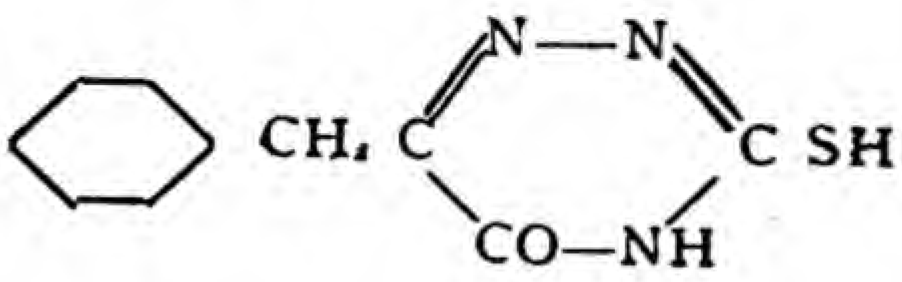
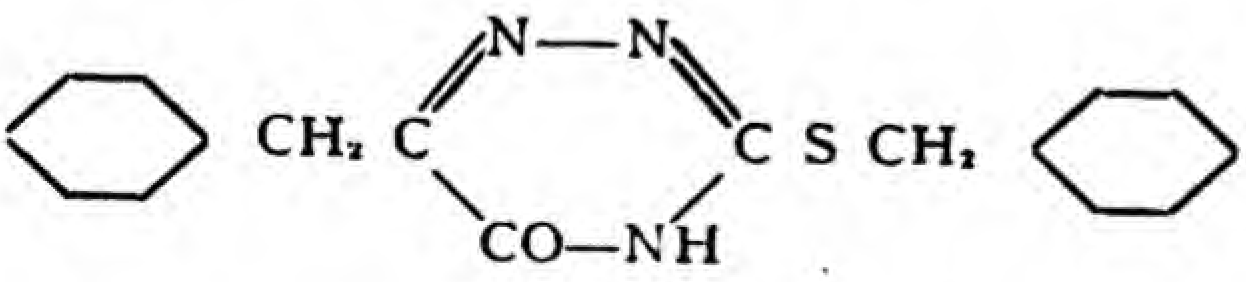
[9] Guenther (to I. G. Farben): German Patent 694,945 (1940); *Chem. Abstracts*, **35**, 5219 (1941).

15. Desulfurization

Considerable work has been carried out on catalytic desulfurization of gasoline, hydrocarbons, organic compounds, and gases. When petroleum fractions are to be hydrogenated, the sulfur must be eliminated as it deactivates the catalyst. The desulfurization of coke oven gas is also a very important industrial process, iron oxides being mostly used.

Cadmium sulfide catalyzes the decomposition of mercaptans at moderate temperature.[1]

By the action of Raney nickel on sulfur compounds when agitating the nickel with the different compounds in aqueous or alcoholic solutions, the sulfur is removed as nickel sulfide with evolution of hydrogen. The results are as follows:[2]

Compound treated		Compounds formed
CS_2	→	Methane
	→	Methane, gaseous ammonia, monoethylamine
	→	Gaseous ammonia, monoethylamine, toluene
$CH_2SH \cdot CH_2SH$	→	Ethane
	→	Benzyldioxytriazine
	→	Benzyldioxytriazine toluene

Based on the fact that Raney nickel, prepared by the usual procedure, contains a considerable amount of hydrogen (43–115 cc hydrogen per gram catalyst), this catalyst was used to cause hydrogenolysis, in the absence of added hydrogen, of a number of sulfur compounds:[3]

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[1] Sabatier, P.: *La Catalyse en Chimie Organique*, Paris, Librairie Polytechnique, 1920, p. 238; Sabatier and Reid: *Catalysis in Organic Chemistry*, New York, D. Van Nostrand Co., 1923.

[2] Bougult, Cattelain, and Chabrier: *Compt. rend.*, **208**, 657 (1939).

$$\underset{\text{Benzyl sulfide}}{C_6H_5CH_2\cdot S\cdot CH_2C_6H_5} \xrightarrow{\text{Ni (H)}} \underset{\text{Toluene (85\% yield)}}{2C_6H_5CH_3}$$

$$\underset{\text{Diphenyl sulfoxide}}{C_6H_5\cdot SO\cdot C_6H_5} \xrightarrow{\text{Ni (H)}} \underset{\text{Benzene (75\% yield)}}{2C_6H_6}$$

Elgin et al.[4] studied the reactions of sulfur compounds present in petroleum, using high-sulfur naphthas in contact with nickel and iron catalysts. These studies were made in vapor-phase at 300 and 400°C and atmospheric pressure, with or without hydrogen, and also in the liquid phase.

In vapor-phase over nickel and iron catalyst, the former was more efficient. It was found that the sulfur may be completely removed in contact with the initially sulfur-free nickel catalyst until the catalyst undergoes decrease in activity as the sulfurization proceeds, and it reaches a state in which it possesses a constant, definite, though reduced activity. The sulfur was removed as hydrogen sulfide. Hydrogen added to the vapor stream tends to increase the extent to which sulfur is removed, and effects the removal of sulfur not affected by the catalyst in its absence.

In the liquid phase, the nickel and iron catalysts do not absorb all the sulfur present in the naphthas.

Elgin[4] also reports studies on prepared sulfur compounds, in hydrocarbon materials, in contact with nickel catalysts, viz.: Naphtha solutions of butyl mercaptan, isobutyl mercaptan, propyl sulfide, isobutyl sulfide, and thiophene. Mercaptans and sulfides, but not thiophene, react with nickel catalyst to evolve hydrogen sulfide in the presence of naphtha vapor. The mercaptans were removed more readily than sulfides, and thiophene was not affected unless hydrogen was added.

In contact with the initially sulfur-free catalyst, thiophene sulfur is removed, but the catalyst rapidly loses its activity toward this compound. The addition of hydrogen, to the naphtha vapor, effects partial removal of thiophene in contact with the catalyst. If the ratio of hydrogen to naphtha is increased, the amount of sulfur removed is increased. Addition of hydrogen effects the removal of a markedly larger proportion of propyl sulfide sulfur than that removed when no hydrogen is added.

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[3] Mozingo, Wolf, Harris and Folkers: *J. Am. Chem. Soc.*, **65**, 1013 (1943).

[4] Elgin et al.: *Ind. Eng. Chem.*, **22**, 1284, 1290 (1930).

The actual data from these experiments are presented in the following tables.

Removal of sulfur from naphtha solutions of individual sulfur compounds at 300°C by a nickel catalyst in steady state, without added hydrogen

Experiment	Sulfur compound in naphtha	Rate of flow cc/hour	Sulfur content Initial %	Sulfur content Final %	Reduction in sulfur %
1	Butyl mercaptan	100	0.375	0.028	93
9	Butyl mercaptan	200	0.375	0.079	79
2	Propyl sulfide	100	0.393	0.309	21
3	Isobutyl mercaptan	100	0.374	0.105	72
4	Thiophene	100	0.389	0.388	0
10	Isobutyl sulfide	100	0.388	0.323	17

Effect of added hydrogen on removal of sulfur from naphtha solution of thiophene and propyl sulfide in contact with a nickel catalyst

Experiment	Sulfur compound in naphtha	Temperature ° C	Naphtha rate cc/hr	Hydrogen flow cc/min	Sulfur content Initial %	Sulfur content Final %	Reduction in sulfur %
1. Catalyst carried to a steady state with butyl mercaptan							
5	Thiophene	300	100	100	0.389	0.360	7.4
6	Thiophene	300	25	200	0.389	0.322	17.2
7	Thiophene	400	100	100	0.349	0.345	11.3
8	Propyl sulfide	300	100	100	0.393	0.137	65.1
2. Catalyst initially sulfur free							
11	Thiophene	300	100	100	0.388	0.350	9.8

Adsorption of sulfur from the liquid phase
(25 g catalyst; 100 cc naphtha)

Sulfur compound in naphtha	Sulfur content Initial %	Sulfur content Final %	Total sulfur adsorbed %
Butyl mercaptan	0.385	0.234	39
Isobutyl mercaptan	0.374	0.242	35
Propyl sulfide	0.406	0.327	19
Thiophene	0.388	0.322	17

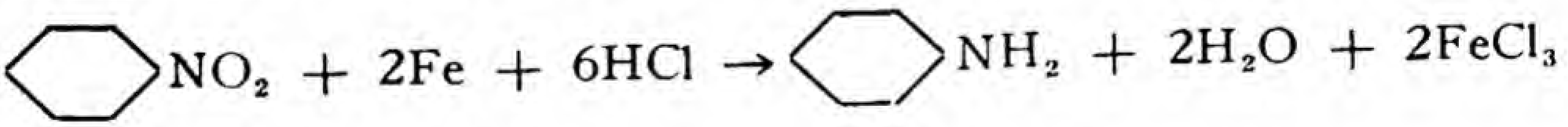
Nickel and cobalt subsulfide catalysts, for decomposing organic sulfur compounds in water or coal gas, are made by soaking a porous catalyst support in a solution of nickel or cobalt sulfate, sulfite, thiosulfate, or sulfamate, drying the resulting mass and converting it to subsulfide by heating at a temperature between 300 and 500°C, by passing water gas through a bed of catalyst, adding the dried impregnated mass to the top of the bed, and removing the converted catalyst from the bottom of the bed.[5]

Flue gases, containing SO_2 are passed through a suspension containing MgO, when $MgSO_3 \cdot 6H_2O$ precipitates at temperatures below 60°C. This sulfite is stable only below 42°C. The crystals are calcined at 900–1000°C, when MgO and SO_2 are formed. The MgO may be used over again and the SO_2 collected for useful purposes. SO_2 may also be oxidized to SO_3 over a MnO_2 catalyst, the rate of formation of SO_3 being proportional to the concentration of SO_2 and to the velocity of the gas.[6]

Gasoline fractions, containing as much as 3–4 per cent by weight of sulfur in the form of organic sulfur compounds (thiophene, thiophanes, thioethers, mercaptans), are desulfurized to contain less than 0.01 per cent sulfur by a catalytic process, using cobalt molybdate as catalyst. In excess of 1500 liquid volumes of feed are desulfurized by one volume of catalyst, without detectable loss of activity. When this catalyst loses activity, it is readily regenerated.[7]

16. Amination *

One of the best known amination processes in the preparation of aniline from nitrobenzene:[1, 2, 3]



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[5] Griffith and Plant: U. S. Patent 2,295,653 (1942).

[6] Peisakhov and Chertov: *J. Chem. Ind. (U.S.S.R.)*, **17**, 6 (1940).

[7] Byrns, Bradley, and Lee: *Ind. Eng. Chem.*, **35**, 1160 (1943).

[1] Wohl: *Ber.*, **27**, 1432, 1815 (1894).

[2] Lyons and Smith: *Ibid.*, **60**, 173 (1927).

[3] Whitney: *J. Am. Chem. Soc.*, **25**, 394 (1903).

* Preparation of amines catalytically.

Using reduced iron in hydrochloric acid, the iron functions as catalyst, and much less acid than the theoretical amount is required to bring about the conversion.

A mixture of vapors of an alcohol and ammonia, when passed over thoria between 300 and 350°C, is dehydrated with the formation of a primary amine:[4]

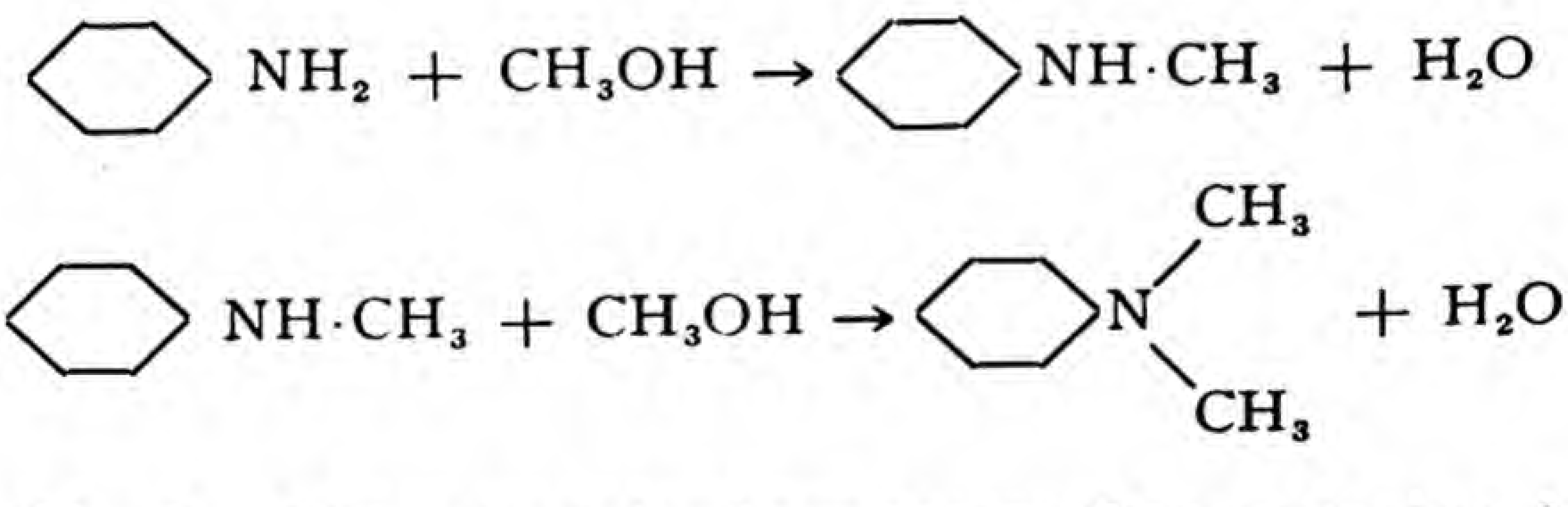
$$C_nH_{2n+1}\cdot OH + NH_3 \rightarrow C_nH_{2n+1}\cdot NH_2 + H_2O$$

If instead of ammonia a primary amine is used, a secondary amine is obtained:

$$C_nH_{2n+1}\cdot OH + R\cdot NH_2 \rightarrow C_nH_{2n+1}\cdot NHR + H_2O$$

Using a secondary amine, a tertiary amine results. Other oxides, e.g., Al_2O_3, may also be used as catalysts, but thoria is the best.

The aromatic amines behave similarly when they are mixed with an alcohol and the mixed vapors are led over aluminum oxide at 350 to 430°C:[5]



Adkins[6] and his associates have prepared many amines by hydrogenation. These reactions have been discussed in this work elsewhere (see page 219) and we will just summarize the reactions here:

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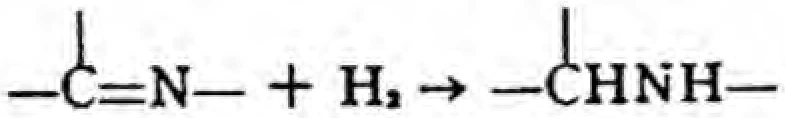
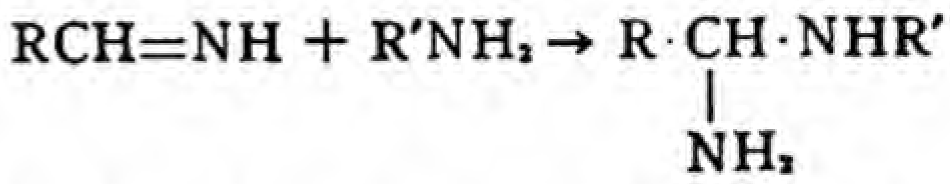
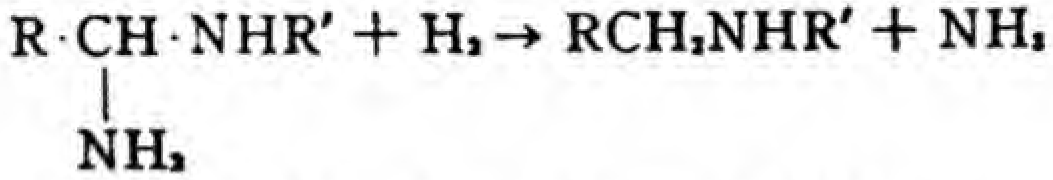
[4] Sabatier and Mailhe: *Compt. rend.*, **148**, 900 (1909).

[5] Ipatieff, W. N., N. Orlow, and A. Petrow: *Aluminiumoxyd als Katalysator in der organischen Chemie*, Leipzig, Akadamische Verlagsgesellschaft, 1929.

[6] Adkins, H.: *Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts*, Madison, The University of Wisconsin Press, 1937.

Preparation of Amines by Hydrogenation

Starting compound	Reaction	Catalyst	Temperature °C	Pressure, atmospheres
1. Cyanides	$RCN + 2H_2 \rightarrow RCH_2NH_2$	Ni (R* and k**)	100–150	100
2. Imines	 $-\overset{\vert}{C}=N- + H_2 \rightarrow -\overset{\vert}{C}HNH-$	Ni (R)	below 80	
3. α-Diamines	(1)  $RCH=NH + R'NH_2 \rightarrow R\cdot\underset{\underset{\textstyle NH_2}{\vert}}{CH}\cdot NHR'$	Cu-Cr*** Ni (R and k)	175 50–100	
	(2)  $R\cdot\underset{\underset{\textstyle NH_2}{\vert}}{CH}\cdot NHR' + H_2 \rightarrow RCH_2NHR' + NH_3$			
4. Oximes	$R_2C=NOH + 2H_2 \rightarrow R_2CHNH_2 + H_2O$	Ni (R)	below 80	
5. Nitro compounds	$RNO_2 + 3H_2 \rightarrow RNH_2 + 2H_2O$	Ni (R) Ni (k) Cu-Cr	25–100 100–110 175	
6. Nitroso compounds	$RNO + 2H_2 \rightarrow RNH_2 + H_2O$	Ni (R) Ni (k)	25 100	
7. Nitrogen-nitrogen bonds	$R_2N-NR_2 + H_2 \rightarrow 2R_2NH$	Ni (k) Ni (R)	80–150	
8. Amides	$RC(O)NR'_2 + 2H_2 \rightarrow RCH_2NR'_2 + H_2O$	Cu-Cr	250–265	200–300

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* R = Raney nickel.

** k = nickel supported on kieselguhr (Adkins' preparation).

*** Cu-Cr = copper chromium oxide.

Glucamines[7] can be prepared from monosaccharides by reacting ammonia or an aliphatic amine with a monosaccharide in the presence of hydrogen and a reducing catalyst such as nickel:

$$CH_2OH(CHOH)_4CHO \xrightarrow[Ni]{NH_3 + H_2}$$

$$CH_2OH(CHOH)_4CH_2{\cdot}NH_2 + H_2O$$

The hydrogen absorption begins at 63 to 65°C, and the temperature increased to 95°C.

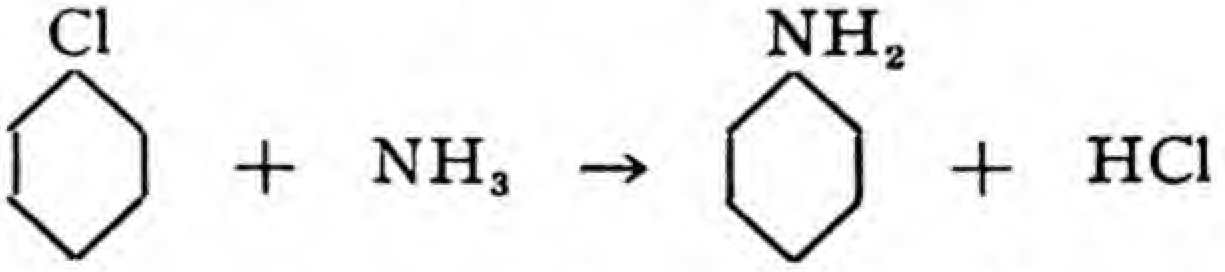
17. Ammonolysis

Reactions of ammonolysis are analogous to those of hydrolysis. Thus, in the ammonolysis of esters, acid amides are formed, in analogy with the formation of the acid from the ester by decomposition with water:[3]

Ammonolysis: $R{\cdot}COOR' + HNH_2 \rightarrow RCONH_2 + R'OH$

Hydrolysis: $R{\cdot}COOR' + HOH \rightarrow RCOOH + R'OH$

Of industrial importance is preparation of aniline by reacting chlorobenzene with an excess of ammonia, using a pressure of 850 to 950 atmospheres, temperatures ranging from 200 to 210°C, and cuprous oxide as catalyst:[1]



This reaction may be carried out in liquid or vapor phase. If the latter is used, a mixed catalyst, consisting of a copper salt and a salt of vanadic, tungstic, or phosphoric acid, is used.[2]

Based on the fact that acids catalyze the hydrolysis of esters, Balaty et al.[3] assumed that ammonium salts should catalyze the ammonolysis of esters in liquid ammonia, because ammonium salts behave as acids in this solvent. This was found to be true as the ammonolysis of glycerides of long-chain fatty acids is catalyzed by the presence of ammonium chloride. Thus, the yields of amides were doubled by adding 4 grams of ammonium chloride to 25 cc of oil (soybean, olive, linseed and pork lard).

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[7] Groggins and Stirton: *Ind. Eng. Chem.*, **29**, 1353 (1937).

[1] Groggins and Stirton: *Ind. Eng. Chem.*, **29**, 1353 (1937).

[2] Mathes and Prahl: U. S. Patent 2,001,281 (1935).

[3] Balaty, Fellinger, and Andrieth: *Ind. Eng. Chem.*, **31**, 280 (1939).

GENERAL REFERENCES

Anderson, Watt et al.: *J. Am. Chem. Soc.*, **63**, 1953 (1941); **64**, 467 (1942); **65**, 49 (1943); **66**, 376 (1944); Andrieth, Scott and Hill, *ibid.*, **64**, 2498 (1942).

18. Enzymes and organic catalysts

Fermentation has been known for centuries, and, in fact, the making of wine, i.e., alcoholic fermentation, was known to the early civilizations of China and Egypt, although this process was not understood before the time of Pasteur. It is also a fact that in our time, in old rural sections and among nomadic people, fermentation is a household process, exercised entirely on the basis of empirical knowledge. In our time, technical catalysis is connected with large mechanical installations, but it is not unreasonable to assume that some future catalytic reactions, using artificial catalysts, will penetrate into the routine of daily life in the same way as fermentation became a routine process centuries ago.

Enzymes are nitrogenous organic catalysts, produced by living organisms, whose functions are of vital importance in the organisms, although the enzymes function in vitro as well. They are usually positive catalysts, the rate of reaction being directly proportional to the enzyme concentration. The enzymes are not very stable, and if they are present in comparatively small amounts only, they finally decompose by autolysis.

In their catalytic action, the enzymes are selective, a certain enzyme being active with a specific compound, or a narrow related group of compounds, only.

The action of enzymes is strongly influenced by the temperature and the acidity or alkalinity of the substrate.[1, 2] Furthermore, the action of enzymes is promoted or inhibited by a variety of sub-

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[1] Sorensen: *Biochem. Z.*, **21**, 131 (1909).

[2] Michaelis: *Ibid.*, **49**, 333 (1913).

stances (co-enzymes and anti-enzymes, respectively) in analogy to the promotion and inhibition of artificial catalytic substances. A characteristic of enzymes is their lability to heat. Most enzyme reactions possess a maximum temperature between 40 and 100°C. At around the freezing point, enzyme action is mostly negligible, and the optimum temperature for most enzymes is between 25 and 40°C.

Enzymes are of colloidal nature, single molecules being of considerable size. The molecular weights of catalases are listed in the following table.

	Molecular weight of catalase[8]
Horse liver	149,800
Cow liver	16,300
Pig liver	89,400
Cow blood	250,300
Horse kidney	320,300

A characteristic of the enzymes is their affinity for other molecules of high molecular weight, such as carbohydrates and proteins. This may, in part, be due to the amphoteric nature of most enzymes. The adsorption of the reacting substances, on the surface of the enzyme, is considered to be preliminary to the chemical reaction between the reactants, the resulting product being desorbed. As long as the reactants are present in reasonable concentration, the adsorption step takes place at very high velocity, due to the specific affinity of the enzyme molecule for the reactants. The actual reaction is probably governed by the law of mass action considered on an activity basis (in the sense of Brönsted's activity concept), and the specific and most critical stage of the enzyme reaction undoubtedly is the desorption of the resulting product. The conditions are similar to those of heterogeneous catalytic action. The affinity of the enzyme for the resulting product complicates enzyme action as comparatively high dilution is required in media converted by enzymes. This factor is of considerable practical interest, as it is desirable to work with high concentrations in industrial work.

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[8] Stern, K. G.: *Medizinische Kolloidlehre*, Dresden, 1933, p. 166. Frankenburger: *Katalytische Umsetzungen und enzymatische Systemen*, Leipzig, Akademische Verlagsgesellschaft, (1937).

The enzymes are named according to their functions, the ending -ase being applied to denote the enzyme according to the product on which it acts.

A very large group of enzymes act as hydrolytic catalysts, and are, as a major group, termed hydrolases. Another large group are the oxidization-reduction enzymes, i.e., oxydases.

Hydrolases

Most enzymes belong to this group. The major subgroups are:

Esterases hydrolyze esters: $R \cdot COO \cdot R' + H_2O \rightleftharpoons R \cdot COOH + R'OH$. The hydrolytic fat-splitting lipases are in this group. The organic catalysts used in technical fat hydrolysis below 100°C according to Twitchell's process (see page 420), act similarly to lipase. The original Twitchell agent is, approximately, of the following composition:

$$COOH \cdot C_{17}H_{34} \cdot (C_{10}H_6) \cdot SO_3H$$

The lipases seem to be less selective than the following hydrolases.

Carbohydrases are active in hydrolysis of carbohydrates. The most important are the enzymes which hydrolyze disaccharides (saccharase, diastase, maltase, etc.), and those which ferment starch (amylase) and cellulose (cellulase).

Glucosidases hydrolyze glucosides and are, consequently, very important as hydrolytic catalysts in plant organisms. In the animal organisms, enzymes of this type hydrolyze nucleic acids. Each variety of these compounds requires a specific enzyme.

Proteases (amidases, peptidases) are enzymes which hydrolyze the —NH·CO— linkage in proteins, polypeptides, and peptides, breaking these compounds down to amino acids. One group of these enzymes hydrolyzes the $—CO—NH_2$ linkage (acid amides), an example of which is the urease which decomposes urea into ammonia and carbon dioxide.

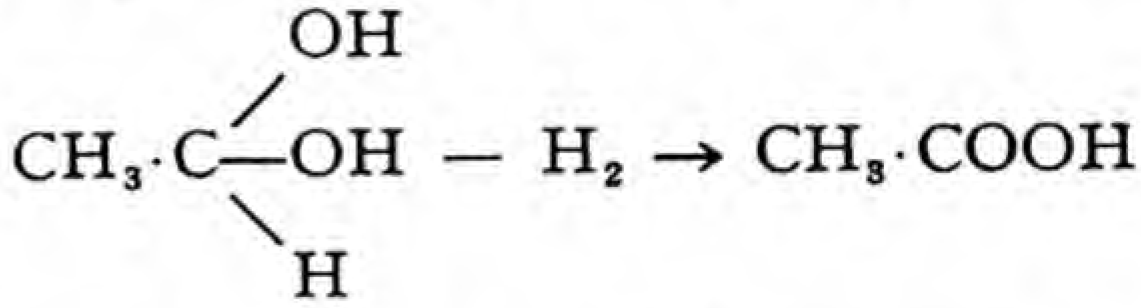
Oxydation-reduction enzymes, or oxido-reductases or dehydrogenases are active without the presence of free oxygen or hydrogen, by transferring oxygen or hydrogen between the molecules in the reaction system itself. This reaction can be expressed generally by the equation:[4]

$$\mathrm{DoH_2 + A \rightarrow Do + AH_2}$$

where $\mathrm{DoH_2}$ is a hydrogen donor which, by splitting off hydrogen, is oxidized to Do. A is a hydrogen acceptor which, by taking up hydrogen, is reduced to the compound $\mathrm{AH_2}$.

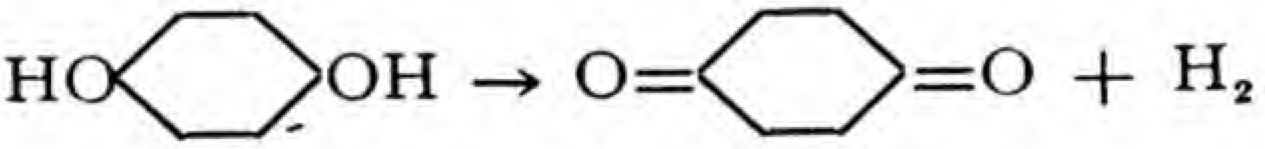
The splitting off of hydrogen may take place without or with a preceding hydration.[4] Some examples are:

1) Oxydation of acetaldehyde to acetic acid takes place by splitting off hydrogen from acetaldehyde hydrate:

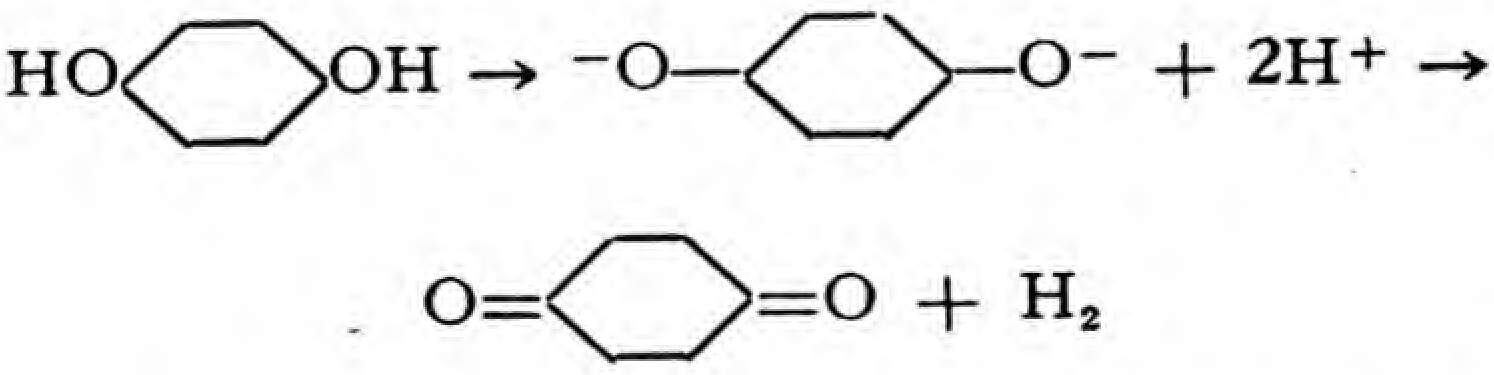


$$\mathrm{CH_3{\cdot}C(OH)(OH)H - H_2 \rightarrow CH_3{\cdot}COOH}$$

2) The oxidation of hydroquinone to quinone is explained as an elimination of hydrogen without preceding hydration:



If this process is considered as a process of splitting off electrons, the reaction scheme is written:[5]



It follows, of course, that this mechanism functions only when the acceptor, A, has greater affinity for hydrogen than the donor, Do.

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[4] Mueller, D.: *Die Oxydationsenzyme und die biologischen Oxydationen*, Copenhagen, Jul. Gjellerup, 1934.

[5] Michaelis, L.: *Oxidation-Reduction Potentials*, p. 51.

Thermodynamically, this means that the energy released by the hydrogenation of A must exceed the energy required for the dehydrogenation of Do. Without catalytic action, this reaction would be very slight. The enzyme activates either the donor or the acceptor, or both, but the true nature of this activation is not known. Processes of this type are considered to comprehend the major oxidation processes in the living organism.

One of the most interesting examples of hydrogen acceptors is free nitrogen which is hydrogenated to ammonia by bacteria in soils (azotobacter), symbiotic bacteria on the roots of leguminoses (bacterium radicicola), or symbiotic fungi on the roots of trees (mykorrhizae).

Oxidases are enzymes which catalyze oxidation of organic compounds by atmospheric oxygen.

Peroxidases cause oxidation by oxygen to peroxides, particularly H_2O_2. The catalases decompose H_2O_2.

Carboxylases are important enzymes in alcohol fermentation. Their function is to split off CO_2 from α-keto acids, e.g., from pyruvic acid, $CH_3 \cdot CO \cdot COOH$, which is decomposed into acetaldehyde and CO_2. The acetaldehyde is then hydrogenated to ethyl alcohol with hydrogen liberated by dehydrogenases.

Saccharase (invertin), in yeast, hydrolyzes sucrose into glucose and fructose.[6, 7]

Alcoholic fermentation consists in hydrolytic decomposition of the higher carbohydrate to ethyl alcohol and carbon dioxide:

$$(C_6H_{10}O_5)_n \xrightarrow{+\,nH_2O} 2nC_2H_5OH + 2nCO_2$$

Phosphates accelerate the conversion of the monosaccharide to alcohol when yeast extract is used. When living yeast cells are used, phosphates have no such action.[8, 9]

Catalase is widely distributed in animal and plant tissues. It

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[6] Euler: *Ber.* 59, 1129 (1926).
[7] Willstätter: *Ibid.*, 59, 1591 (1926).
[8] Harden and Young: *Biochem. J.*, 1216 (1927).
[9] Schmidt: *Z. Elektrochem.*, 39, 969 (1933).

acts specifically on the decomposition of hydrogen peroxide, but does not catalyze the decomposition of other peroxides.

Finally attention should be called to the striking similarity between the action of enzymes and that of artificial organic catalysts, a matter which has been discussed in detail by Langenbeck[10] and Frankenburger.[11] Some examples of the action of organic catalysts have been presented at different places in this text, and only one striking example will be discussed here.

Langenbeck et al.[10] have shown (by systematic substitution of carboxylase models) that a twice-substituted organic catalyst molecule is twice as active as one which is substituted only once and so on. The active group of such a catalyst is the one which reacts directly with the substrate to be converted. The activating groups are those which increase the reactivity of the active group without changing during the conversion.

Examples are groups such as carboxyl, nitro, halogen, etc.; a methyl group in close proximity to such a group is reactive, but less or not at all if it is moved farther away.

In the following table is given an example of carboxylase models illustrating these principles, the activity values being the number of mols of phenylglyoxylic acid decomposed by one mol catalyst in the first five minutes at the temperature given:[10]

Catalyst	Temperature of reaction °C	Activity value
Methyl amine $CH_3 \cdot NH_2$	137	0.25
Ethyl amine $CH_3 \cdot CH_2 \cdot NH_2$	137	0.25
β-amino butyric acid $CH_3 \cdot CH(NH_2) \cdot CH_2 \cdot COOH$	137	0.47

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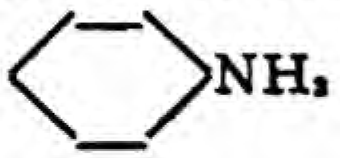
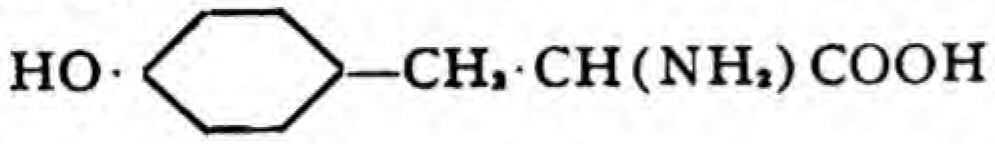
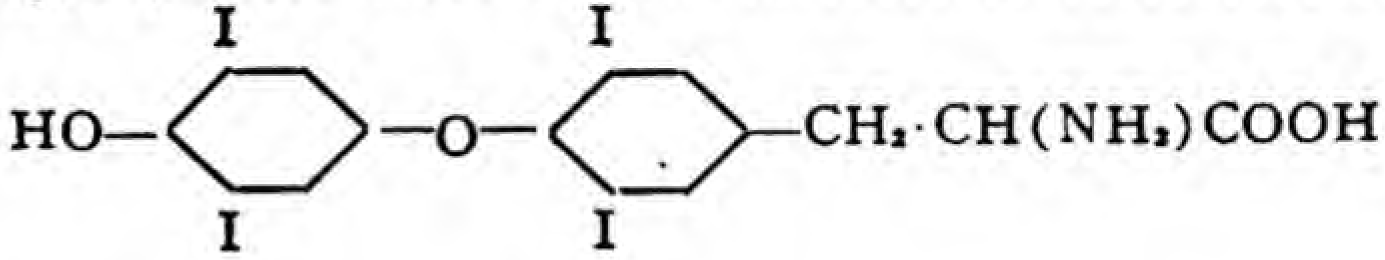
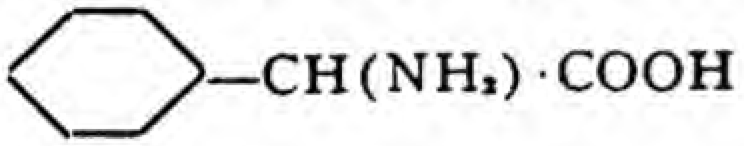
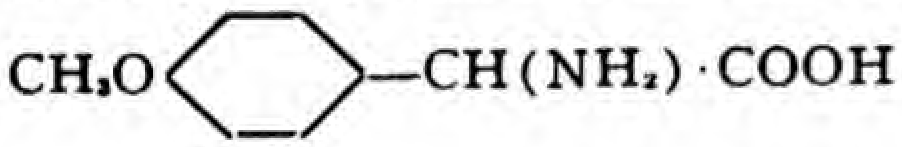
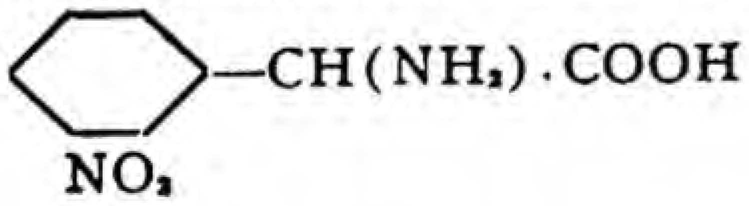
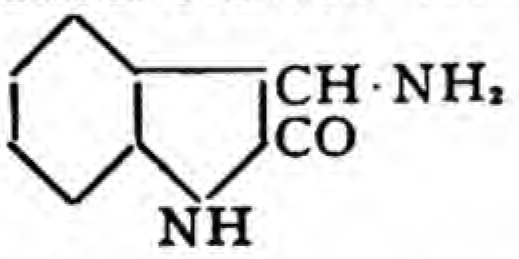
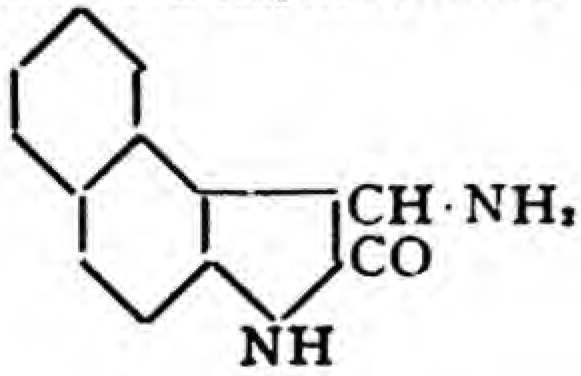
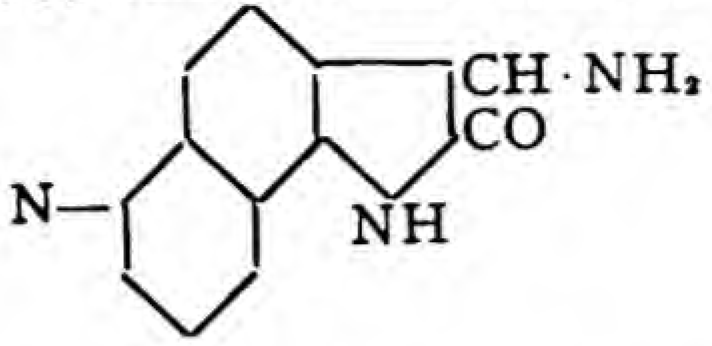
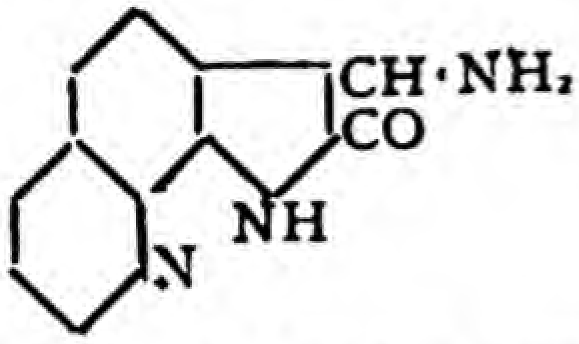
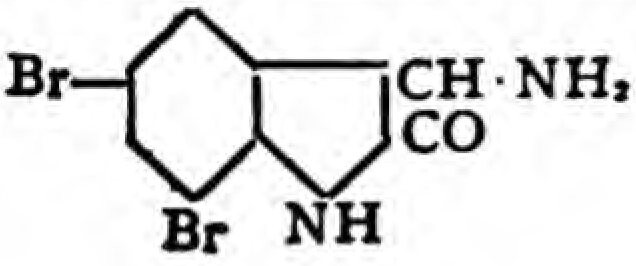
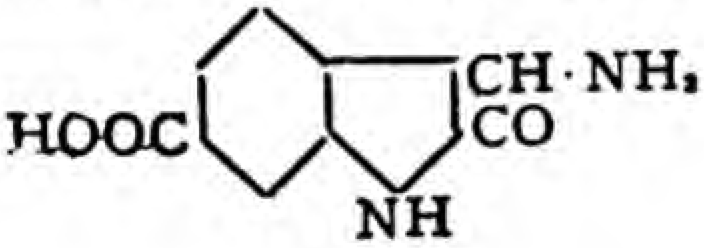
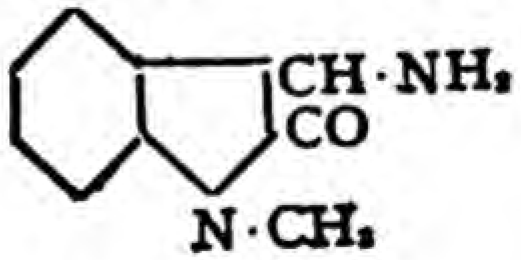
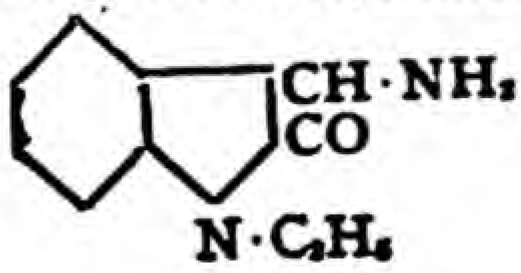
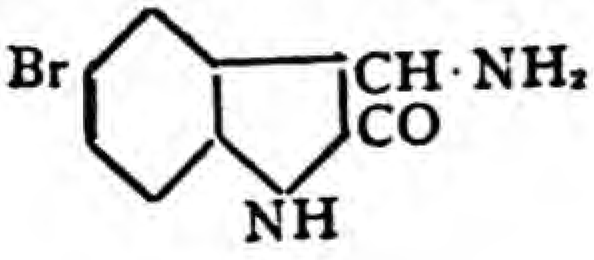
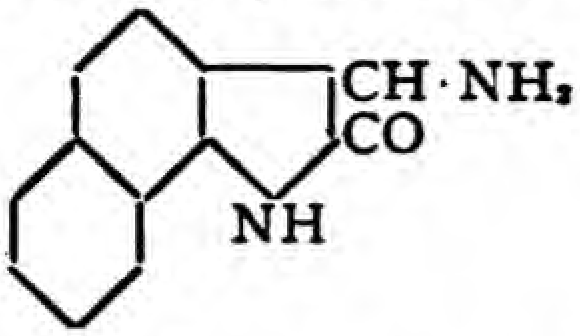
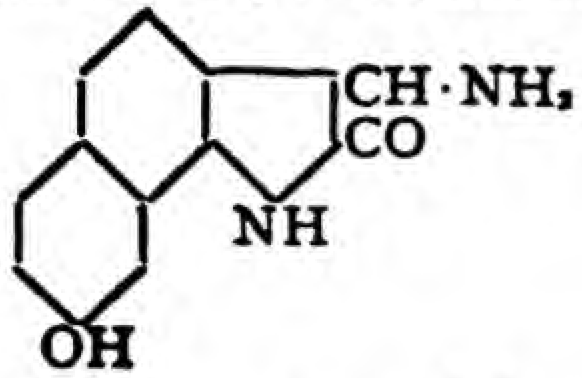
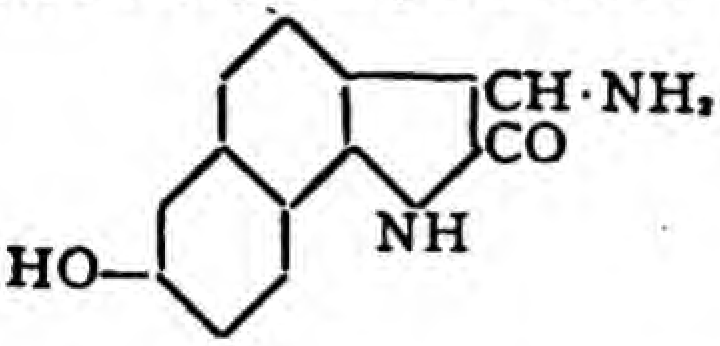
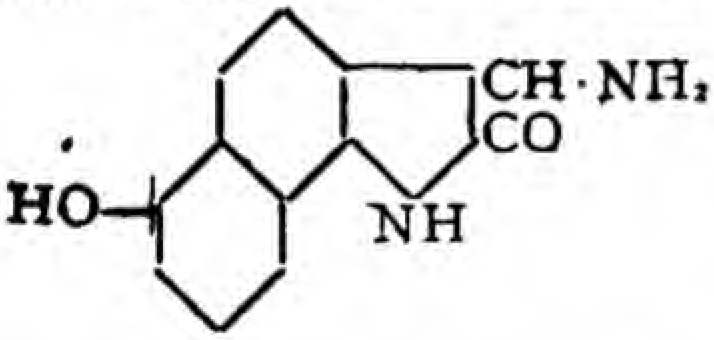
[10] Langenbeck, W.: *Die organischen Katalysatoren und ihre Beziehung zu den Fermenten,* Berlin, Verlag von Julius Springer, 1935; Langenbeck, Hutschenreuter, and Jüttemann: *Liebigs Ann. Chem.,* **499,** 53 (1931); Langenbeck, Jüttemann and Hellrung: *Ibid.* **512,** 276 (1934); Langenbeck: *Z. angew. Chem.,* **45,** 97 (1932); Ergebnisse Enzymforschung **2,** 314 (1933).

[11] Frankenburger, W.: *Katalytische Umsetzungen und enzymatische Systeme,* Leipzig, Akademische Verlagsgesellschaft, 1937.

Aniline 	137	1.65
Glycocoll $CH_2(NH_2)\cdot COOH$	137	4.65
α-amino-isobutyric acid $(CH_3)_2C(NH_2)\cdot COOH$	137	1.5
Tyrosin 	137	5.70
Thyroxin 	100	2.7
Alanin $CH_3\cdot CH(NH_2)\cdot COOH$	137	6.5
Phenyl-amino acetic acid 	100	3.2
p-methoxy-phenylamino acetic acid 	137	7.0
m-nitro-phenylamino acetic acid 	137	10.8
3-amino-oxindole 	70	6.5
3-amino-α-naphthoxindol 	70	0.15

6,7-pyridino-3-amino-oxindol 	37	0.15
7,6-pyridino-3-amino-oxindol 	37	0.17
5,7-dibromo-3-amino-oxindol 	100	17.2
3-amino-oxindol-6-carbonic acid 	100	18.0
1-methyl-3-amino-oxindol 	100	60
1-phenyl-3-amino-oxindol 	70	5.3
5-bromo-3-amino-oxindol 	70	7.4

3-amino-α-naphthoxindol	37	0.64
		
3-amino-8-oxy-α-naphthoxindol	37	0.20
		
3-amino-7-oxy-α-naphthoxindol	37	0.79
		
3-amino-6-oxy-α-naphthoxindol	37	1.48
		

One gram of the most active carboxylase catalyst (1-methyl-3-amino-oxindole) decomposed at 37°C in one minute 1.25 millimols of keto-acid, and one gram of crystallized pepsin (Northrop) decomposes at 35.5°C in one minute 28 millimols of peptides. Thus, the natural enzyme is 22 times as active as the best organic catalyst in this series. However, the activity values by systematic activation increased from 0.15 to 60, i.e., 400 times, and the possibility of finding an organic catalyst of the same efficacy as the pepsine is very good indeed.

CHAPTER V

INDUSTRIAL CATALYTIC REACTIONS

1. Catalytic reactions in the synthetic nitrogen industry

The synthetic nitrogen industry is only about 50 years old, but it has, as it is well known, grown to very considerable dimensions.

From an American point of view, the magnitude of and national interest in this vital industry is described in Report No. 114, Second Series, Washington, 1937; Chemical Nitrogen (United States Tariff Commission).

Nitrogen oxides

Nitrous oxide, N_2O, is formed when NH_3 is mixed, over a catalyst, with an excess of oxygen, or gases containing oxygen, at temperatures between 200 and 500°C. N_2O can, in this way, be made by a continuous process. As catalyst, MnO_2 containing Fe_2O_3 or Bi_2O_3 can be used. This catalyst, at 300°C, provides about 90% conversion of the NH_3 into N_2O.[1]

N_2O may also be produced by heating NH_4NO_3 to its decomposition temperature in the presence of 0.001–2 per cent of H_3PO_4, $NH_4H_2PO_4$, $(NH_4)_4P_4O_{12}$, Na_3PO_4, Na_2HPO_4, $Ba_2P_4O_7$, $BaPO_3$, $MgHPO_4$, P_2O_5, As_2O_3, $AgNO_3$, $Mn(NO_3)_2$, or $(NH_4)_2MoO_4$.[2]

Iodine, chlorine, bromine, nitric oxide,[3] and copper oxide[4] catalyze the decomposition of nitrous oxide. The kinetic theory, involved in the decomposition of nitrous oxide and the other nitrogen oxides, has been discussed in detail by Schumacher,[5] Hinshelwood,[6] and Kassel.[7]

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[1] Nagel: *Z. Elektrochem.*, **36**, 754 (1930).

[2] Dupont de Nemours & Co., E. I., British Patent 510,889 (1939).

[3] Musgrave and Hinshelwood: *Proc. Roy. Soc.*, A **135**, 23 (1932).

[4] Schwab and Schultes: *Z. phys. Chem.*, **B 9**, 265 (1930).

Nitric oxide, NO, is formed by the direct combination of nitrogen and oxygen at high temperatures:

$$N_2 + O_2 \rightleftarrows 2NO - 43{,}000 \text{ cal.}$$

This reaction does not proceed appreciably to the right below 1450°C.

N_2 and O_2 dissociate increasingly with increase in the temperature.[8] The atomic reaction: $N + O \rightarrow NO$, is strongly exothermic (123,000 cal.); consequently, the formation of NO by the atomic process decreases with rising temperature. For calculation of the equilibrium at higher temperatures, the following reactions must be considered:

1. $N_2 \rightleftarrows N + N$
2. $O_2 \rightleftarrows O + O$
3. $N_2 + 2O \rightleftarrows 2NO$
4. $O_2 + 2N \rightleftarrows 2NO$
5. $N_2 + O_2 \rightleftarrows 2NO - 43{,}000$ cal.
6. $N + O \rightleftarrows NO + 123{,}000$ cal.

The thermal ionization of N_2 and O_2 is not of practical importance as it takes place above 9000°C.

Nitrogen trioxide, N_2O_3, which is the anhydride of nitrous acid, is formed according to:[9]

$$NO + NO_2 \rightleftarrows N_2O_3 + 9{,}600 \text{ cal.}$$

Nitrogen dioxide, NO_2, is formed according to the equation:

$$N_2O_4 \rightleftarrows 2NO_2 - 13{,}000 \text{ cal.}$$

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[5] Schumacher, H. J.: *Chemische Gasreaktionen,* Dresden, Theodor Steinkopff, 1938.

[6] Hinshelwood, C. N.: *Kinetics of Chemical Change in Gaseous Systems,* New York, Oxford Press, 1933, p. 167.

[7] Kassel, L.: *The Kinetics of Homogeneous Gas Reactions,* Am. Chem. Soc. Monograph, New York, Reinhold Publishing Corp., 1932.

[8] Briner: *Compt. rend.,* **155**, 1149 (1912); *ibid.,* **157**, 281 (1913).

[9] Bodenstein: *Z. phys. Chem.,* **100**, 68 (1900).

Industrially, NO_2 is made by oxidation of NO according to:

$$2NO + O_2 \rightleftarrows 2NO_2 + 2{,}650 \text{ cal.}$$[10, 11]

This reaction proceeds readily at ordinary temperature which is noted by the brown fumes of NO_2.

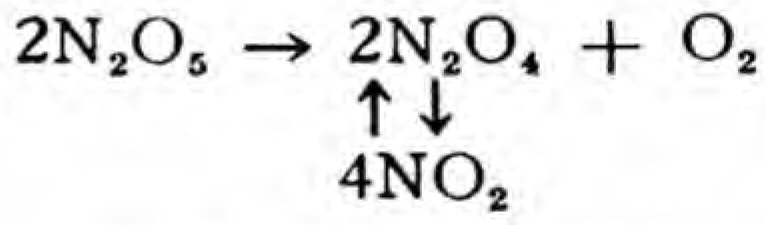
The velocity of this reaction is increased by catalysts such as activated carbon of high adsorptive power, e.g., from cocoa nuts,[12] silica gel and alumina gel.

Contradictory views are held as to the necessity of the presence of water in the formation of NO_2 from NO and O_2.[13, 14] The action of H_2O in homogeneous oxidation of NO is ascribed to the fact that only the NO-molecules associated with H_2O-molecules take part in the reaction.[14] However, this point requires further investigation.

The reaction mechanism is suggested to be as follows: [15, 16, 17, 18]

1. $NO + O_2 \rightleftarrows NO_3$ (equilibrium with high velocity)
2. $NO_3 + NO \rightleftarrows 2NO_2$ (determines the velocity)

Nitrogen pentoxide, N_2O_5, which is the anhydride of nitric acid, decomposes thermally as follows (unimolecular reaction): [19]



$$\begin{array}{ccccc} 2N_2O_5 & \rightarrow & 2N_2O_4 & + & O_2 \\ & & \uparrow\downarrow & & \\ & & 4NO_2 & & \end{array}$$

The velocity of this reaction does not seem to be influenced by catalysts.

Up to 1925, this was the only known gaseous unimolecular

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[10] Lunge: *Ber.*, **18**, 1384 (1885).

[11] Lunge and Berl: *Z. angew. Chem.*, **19**, 857 (1906).

[12] Burdick: *J. Am. Chem. Soc.*, **44**, 244 (1922).

[13] Baker: *J. Chem. Soc.*, **65**, 611 (1894).

[14] Hasche: *J. Am. Chem. Soc.*, **48**, 2253 (1926).

[15] Blick: *Z. angew. Chem.*, **23**, 2017 (1910).

[16] Bodenstein: *Z. phys. Chem.*, **100**, 68 (1922).

[17] *Gmelins Handbuch der anorganischen Chemie*, 8th Ed., Berlin, Verlag Chemie, 1936, Nitrogen System No. 7.

[18] Raschig: *Z. angew. Chem.*, **17**, 1777 (1904).

[19] Linhorst: *J. Am. Chem. Soc.*, **56**, 836 (1934).

reaction. Hinshelwood[6] explains the reaction mechanism as proceeding through the following steps:[6, 20]

$$\begin{array}{ll} 1. & N_2O_5 \rightarrow N_2O_3 + O_2 \text{ instantaneous} \\ 2. & N_2O_3 \rightarrow NO + NO_2 \text{ instantaneous} \\ 3. & NO + N_2O_5 \rightarrow 3NO_2 \\ \hline & 2N_2O_5 \rightarrow 4NO_2 + O_2 \end{array}$$

Nitrogen trioxide, NO_3, is produced when nitrogen pentoxide reacts with ozone, without taking part in the thermal reaction.[21, 22, 23]

Synthesis of ammonia

The synthesis of ammonia proceeds catalytically as follows:[17, 24, 25]

$$\underset{\frac{1}{2}\text{ volume}}{\tfrac{1}{2}N_2} + \underset{1\frac{1}{2}\text{ vol.}}{\tfrac{3}{2}H_2} \rightleftarrows \underset{1\text{ vol.}}{NH_3} + 10{,}629 \text{ cal. } (1 \text{ atm., } 0°\text{C})$$

The process being reversible, it is never complete.

The equilibrium constant is calculated according to:

$$Kp = \frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}} \cdot P_{N_2}^{\frac{1}{2}}}$$

The equilibrium concentrations, as depending on the temperature, are calculated by Haber[26] as follows for pressures up to 500 atmospheres:

$$\log Kp = 2098.2/T - 2.509 \log T - 1.006 \times 10^{-4}T + 1.859 \times 10^{-7}T^2 + 2.10$$

The concentrations of NH_3, at different temperatures and pressures, according to this equation, are as follows:

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[20] Busse and Daniels: *J. Am. Chem. Soc.*, **49**, 1257 (1927).
[21] Daniels and Johnston: *J. Am. Chem. Soc.*, **43**, 53 (1921).
[22] Kassel: *Ibid.*, **50**, 1344 (1928).
[23] Schumacher and Sprenger: *Z. phys. Chem.*, **136**, 77 (1928).
[24] Berthelot: *Compt. rend.*, **140**, 1153 (1905).
[25] Haber and van Oordt: *Z. anorg. allgem. Chem.*, **43**, 111 (1905).
[26] Haber: *Z. Elektrochem.*, **20**, 597 (1914).

Absolute temperature °K	Equilibrium concentration, per cent					Kp
	1 atm.	10 atm.	30 atm.	100 atm.	200 atm.	
473	15.3	51.6	67.6	80.6	85.8	0.660
573	2.18	16.0	31.8	52.1	62.8	0.070
673	0.44	4.1	10.7	25.1	36.3	0.138
773	0.129	1.3	3.62	10.4	17.6	0.0040
873	0.049	0.5	1.43	4.47	8.25	0.00151
973	0.0223	0.21	0.66	2.14	4.11	0.00069
1073	0.0117	0.12	0.35	1.15	2.24	0.00036
1173	0.0069	...	0.21	0.68	1.34	0.000212
1273	0.0044	...	0.13	0.44	0.87	0.000136

At higher pressures, i.e., 200 to 1000 atm., more NH_3 is formed than expressed by the equation above, which is ascribed to the use of more efficient catalysts ($Fe—Al_2O_3—K_2O$). At still higher pressures, i.e., 2000 to 4000 atm. and temperatures of 400 to 1200°C, no special catalyst is required, as the walls of the converter act as catalyst. By charging the converter with iron filings and asbestos, better results are obtained than without this, as almost all substances act as contact catalysts under these conditions. Contact poisons, such as H_2S and CO, are not active under these conditions.[27, 28, 29]

The relationship between the rate of flow of the gases and the NH_3 produced per liter catalyst space per hour, at 515°C and 114 atm., using a uranium carbide catalyst, was as follows:[29a]

Liter gas per liter catalyst space per hour	5,800	31,650	82,600	194,000
Percentage (volume) of NH_3 produced	7.63	6.42	4.78	4.18
Kilograms of NH_3 per hour per liter	0.318	1.46	2.84	5.83

It has been established that both the nitrogen and the hydrogen must be in the atomic state in order that the NH_3 is synthesized.[30, 31] It is assumed that the active catalyst surface transforms the molecular gases, in the adsorptive layer, to atomic ones. If active nitro-

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[27] Basset: French Patent 771,306 (1933).

[28] Basset: *Compt. rend.*, **199**, 205 (1934).

[29] Acker: U. S. Patent 1,050,902 (1911).

[29a] Haber and Hinshelwood: *Z. Elektrochem.*, 21, 241 (1915).

[30] Langmuir: *J. Am. Chem. Soc.*, **34**, 1324 (1912).

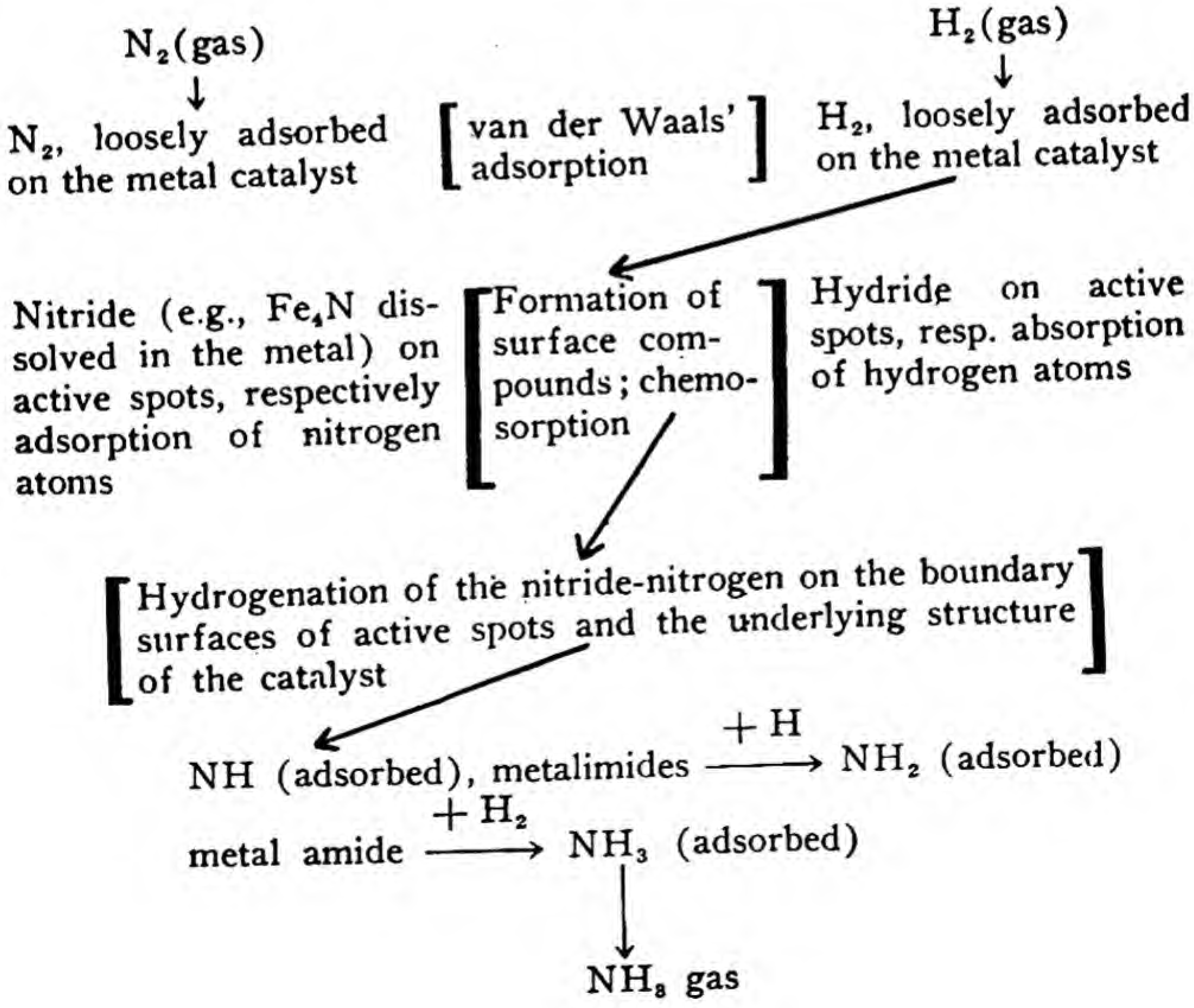
[31] Strutt: *Proc. Roy. Soc.*, A **85**, 224 (1911).

gen reacts with molecular hydrogen, H_2, hydrazine, NH_2NH_2 is formed.[32] However, this reaction is practically suppressed with the catalysts used in the manufacture of ammonia.

It has also been suggested that the contact synthesis of NH_3 is due to gradual hydrogenation of the nitrides formed on the surface of the catalyst:[33]

$$M_xN \quad M_xNH \quad M_xNH_2 \quad M_xNH_3 \quad M_x \quad NH_3 .$$

According to this theory, the rate of formation of the nitride, on the surface of the catalyst, is the factor determining the rate of the reaction.[34, 35, 36] These mechanisms have been thoroughly discussed by Frankenburger[37] and Emmett,[38, 39] and for detailed study these references are recommended. Frankenburger[37] summarizes the ammonia synthesis by the following scheme:


N_2(gas)
H_2(gas)
N_2, loosely adsorbed on the metal catalyst
van der Waals' adsorption
H_2, loosely adsorbed on the metal catalyst
Nitride (e.g., Fe_4N dissolved in the metal) on active spots, respectively adsorption of nitrogen atoms
Formation of surface compounds; chemosorption
Hydride on active spots, resp. absorption of hydrogen atoms
Hydrogenation of the nitride-nitrogen on the boundary surfaces of active spots and the underlying structure of the catalyst
NH (adsorbed), metalimides
+ H
NH_2 (adsorbed)
metal amide
+ H_2
NH_3 (adsorbed)
NH_3 gas

The kinetics of ammonia synthesis has been studied extensively in the past,[37, 41] and more recently by Emmett et al.,[38, 39, 42] and Temkin and Pyzhev.[43] The latter have developed a set of equations which, according to Emmett and Kummer [42] are well in accordance with experimental facts.

Of the single catalysts for ammonia synthesis, osmium is the best. Iron, molybdenum, uranium, nickel, cobalt, manganese, palladium and platinum are other single metal catalysts investigated. However,[25, 44, 45, 46, 47] it was soon found that mixed catalysts are superior to single ones.

In studying the formation of the nitrides of barium, titanium, silicon and aluminum, it was observed that the nitrogen, as a rule, was fixed faster and to a larger extent in the presence of foreign materials.[47, 48] Since this important work was undertaken, many observations have been published, the Fe-Al_2O_3-K_2O contact mass being favored, in which iron forms the major part. The presence of the K_2O increases the adsorption of the hydrogen and nitrogen, and the Al_2O_3 prevents sintering of the iron atoms on the surface.

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[32] Steiner: *Z. Elektrochem.*, **36**, 810 (1930).

[33] Frankenburger: *Z. phys. Chem.*, Bodenstein Festband, (1931).

[34] Messner and Frankenburger: *Z. phys. Chem.*, Bodenstein Festband (1931).

[35] Mittasch, Kuss, and Emert: *Z. Elektrochem.*, **34**, 829 (1928).

[36] Taylor and Jungers: *J. Amer., Chem. Soc.*, **57**, 660 (1935).

[37] Frankenburger: *Z. Elektrochem.*, **39**, 45, 50, 97, 818 (1933).

[38] Emmett, P. H.: Synthetic Ammonia, Chapter VIII of H. A. Curtis: *Fixed Nitrogen*, Am. Chem. Soc. Monograph, New York, Reinhold Publishing Corp., 1932, p. 150.

[39] Emmett, P. H.: *The Synthesis of Ammonia*, Twelfth Report of the Committee on Catalysis, National Research Council, New York, John Wiley & Sons, 1940, p. 138.

[41] Benton: *Ind. Eng. Chem.*, **19**, 496 (1927).

[42] Emmett and Kummer: *Ind. Eng. Chem.*, **35**, 677 (1943).

[43] Temkin and Pyzhev: *Acta Physicochim. (U.S.S.R.)*, **12**, 327 (1940).

[44] German Patents 249,447, 254,437, 258,146, 262,823 (1910), 261,507, 286,430 (1911) and 276,133 (1912).

[45] Haber and Le Rossignol: *Ber.*, **40**, 2144 (1907); *Z. Elektrochem.*, **14**, 181 (1908).

[46] Kunsman: Physical Methods of Studying Chemically Active States of Gases and of Investigating Catalyst Surfaces, Chapter VI of H. A. Curtis: *Fixed Nitrogen*, New York, Reinhold Publishing Corp., 1932.

[47] Mittasch: *35th. Meeting of the Bunsen Society for Applied Physical Chemistry, Heidelberg*, Berlin, Verlag Chemie, 1930.

[48] Mittasch: *Ber.*, **59**, 15 (1926).

Many other catalysts have been suggested for ammonia synthesis.[17, 26, 37, 38, 39, 44, 49]

Catalyst poisons are phosphorus, arsenic, sulfur and carbon monoxide. As a rule, the poisoning effect increases as the temperature is lowered. At very high pressures (2-5000 kg per cm^2), poisons seem to have little or no effect.[50]

As to the activity of the iron catalyst, the extent of the active center has been studied by the following reaction:

$$\underset{\text{surface}}{3Fe} + 4H_2O \rightleftarrows \underset{\text{surface}}{Fe_3O_4} + H_2O$$

The quantity of oxide formed is a measure for the activity. Almquist [51] made the interesting discovery that in chemically pure iron one of 2000 iron atoms is active, whereas in iron of technical purity one of 200 iron atoms is active. A very good discussion of the activity of ammonia catalysts has been published by Kunsman.[46]

Manufacture of ammonia

The raw materials are nitrogen from the air, hydrogen, catalyst, and power. The major cost, involved in developing these processes technically, and operating them on an industrial scale, is that of handling large volumes of gases which have to be separated, purified and compressed.

The nitrogen may be obtained by fractional distillation of liquefied air, from producer gas, or by burning the oxygen out of the air by means of hydrogen, molten metals, hot contact masses of oxidizable metals,[52] and, in the last two cases, regenerating with water gas.[29]

In some of the largest synthetic ammonia plants in Europe, the original success was achieved by mixing producer gas and water gas in the proper proportions for synthesis of ammonia. A mixture of steam and air is passed into a bed of incandescent coke or lignite

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[49] Mittasch: *Z. Elektrochem.*, **36**, 569 (1930).

[50] Basset: *Compt. rend.*, **199**, 205 (1934); *Bull. soc. chim.*, (5), **2**, 108 (1935).

[51] Almquist: *J. Am. Chem. Soc.*, **48**, 2820 (1926).

[52] Beckmann: U. S. Patent 1,007,516 (1909).

of low sulfur content in order to obtain a mixture of producer gas and water gas, the proportions of which are regulated to suit the requirements of ammonia synthesis.

Percentage composition of producer and water gas
(Report No. 114, page 344)

	N	H	CO	CO_2
Producer gas	51	14	26	9
Water gas	3.5	48	42	6.5

The H_2S is removed over activated carbon or another purifier and then, the mixture is brought to react with iron oxide at atmospheric pressure, at 500°C, and in the presence of excess steam. Thus, the CO is converted into CO_2 ($CO + H_2O \rightleftarrows CO_2 + H_2$), which is removed by scrubbing with water. The last traces of H_2S and CO, and the CO_2, are removed and the gas, consisting of nitrogen, hydrogen, argon, and a little methane (formed by the gasification of the coke) is dried. If required, this mixture is adjusted with nitrogen from liquefied air.

Other sources of hydrogen for ammonia synthesis are presented in the following table:

Percentages of synthetic ammonia produced from hydrogen derived from the following sources—(fertilizer year)
(Report No. 114, page 341)

	1926–27	1929–30	1933–34
1. Water gas	89.0	69.7	57.0
2. Coke-oven gas	3.0	14.2	25.0
3. Electrolysis of water	6.4	15.2	16.0
4. Electrolysis of brine, fermentation, natural gas, etc.	1.6	0.9	2.0
Total	100.0	100.0	100.0

The Haber-Bosch process[53] (Report No. 114, page 341) is the first process for ammonia synthesis to be used commercially. It is based on Fritz Haber's classical researches (1903–1907), and was developed technically by C. Bosch and A. Mittasch. The catalyst used is made from metallic iron and contains Al_2O_3 and

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[53] Bosch: *Chem. Fabrik*, 6, 127 (1933).

K_2O. The purified gas (in some big works a mixture of producer and water gas as described above) enters the reaction apparatus under a pressure of 200 atmospheres, and from 15 to 25 volume per cent of the gas mixture (8 per cent per pass) is converted into ammonia at a temperature of 500°C and 200–300 atmospheres pressure, and a time of contact between gas and catalyst of the order of magnitude of 20 seconds. Originally the ammonia was absorbed in water; but it is now liquefied.

The Claude process[54, 55, 56] is distinguished by the high pressure and temperature used, and that no recirculation of the unconverted gases is used:

Pressure-atm.	Temperature, °C	Volume-velocity, Catalyst volume, per hour
900–1,000	500–650	80,000–100,000

The catalyst is made by burning metallic iron with an excess of oxygen to Fe_3O_4, and then reducing the oxide with hydrogen. About one per cent of CaO or MgO is added to the iron oxide. As a source of hydrogen, coke-oven gas, water gas, or electrolytic hydrogen is used. Four converters are used, two parallel and two in series, and 80–85 per cent of the N-H mixture is converted, without recirculation. Due to the high temperature, the catalyst rapidly loses its activity and must be replaced in a week or two. The installation costs are high.

The Casale process is used extensively in Japan, France, Belgium, and Italy. Pressures of 750 to 800 atmospheres, a temperature of about 450°C, volume velocities of 16,000 to 25,000, and times of contact of 13.5 to 19 seconds occur in the process, and the conversion is from 16 to 25 volume per cent per pass, with up to about 99 per cent yield. Only one converter is used, and the gas is recirculated frequently in order to protect the catalyst from overheating.

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[54] Claude: *Compt. rend.*, **169**, 649, 1039 (1919); *ibid.*, **170**, 174 (1920); *ibid.*, **172**, 442 (1921); *ibid.*, **174**, 157, 681 (1922); *Bull. soc. chim.* **27**, 705 (1920).

[55] Claude: British Patents 130,086 (1918), 131,870 (1919) and 161,195 (1921); *Z. angew. Chem.*, **43**, 417 (1930).

[56] Moldenhauer: *Chem. Ztg.*, **48**, 233 (1924).

The catalyst is made from iron turnings, to which activators are added, oxidized by a current of oxygen in a crucible yielding a mass of a composition somewhat like that of magnetite. The mass is then reduced. Originally, only electrolytic hydrogen was used in this process, but it has now been designed for use of coke-oven gas and water gas.[57] (Report No. 114, page 341.)

The Fauser process[58, 59, 60] operates at 200 to 250 atmospheres pressure, depending on whether the ammonia is to be obtained in the gaseous or liquid form. The temperature, in the upper part of the converter, is about 550°C and in the lower part about 450°C. The reaction, in the upper part of the converter, allows for higher velocity, and in the lower part for higher concentration of NH_3. The time of contact, in the lower part of the converter, is about 20 seconds, about 16 per cent NH_3 being formed at 250 atmospheres. The ammonia is cooled and tapped off in anhydrous liquid form. The reacting gases are recirculated. This process was originally designed for use of electrolytic hydrogen; but a suitable gas mixture may be made by gasification of carbon with steam and air under pressure.

The Mont Cenis (Uhde) process[61] is characterized by the use of low operating pressures (90 to 100 atmospheres) and a very active catalyst consisting of complex ferrocyanides prepared in an acetic anhydride solvent. The gases used are passed through molten alkali metal amides at 200 to 300°C, under pressure. The reaction temperature in the converter, is from 350 to 430°C. The purity of the gases and arrangements for prevention of overheating of the catalyst provide for its long life. The ammonia is recovered, in the liquid form, by refrigeration of the reaction gases, which are recirculated. The recovery in the pass is from 9 to 25 per cent.

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[57] Casale: U. S. Patents 1,408,987 (1922) and 1,447,123 (1923); British Patents 197,199 (1923), 227,491 (1925), 231,417 (1925) and 233,040 (1925).

[58] Fauser: U. S. Patent 1,487,647 (1924); British Patents 240,436 (1926), 292,129 (1928), 313,446 (1930) and 442,574 (1936).

[59] Fauser: *Chem. Met. Eng.*, **39**, 430 (1932).

[60] Fauser: *Chimie & industrie*, **25**, 556 (1931).

[61] Uhde: British Patents 247,225 (1925), 247,226 (1926), 253,122 (1927), 259,230 (1927), 272,930 (1929), 272,929 (1928); Canadian Patent 283,221 (1928).

The American process[62, 63, 64] (Report No. 114, page 341) was developed by the Fixed Nitrogen Laboratory of the United States Department of Agriculture. The source of hydrogen is (as in the Haber-Bosch process) a mixture of producer gas and water gas, the CO being converted catalytically into CO_2, which is scrubbed out with water. However, any other source of hydrogen, and nitrogen obtained by liquefaction of air, may also be used. The pure gas mixture is converted in contact with a catalyst at 475°C and 300 atm. pressure.[65]

The catalyst consists of iron oxide granules, containing 3 per cent Al_2O_3 and 1 per cent K_2O, which are prepared by burning pure iron in oxygen, and fused in an electric furnace, in a crucible whose hearth is made of natural magnetite. The promotors are added to the fused mass, which is cooled, and crushed to give granules of uniform size. In the converter, the hydrogen reduces the iron oxide, porous granules being left. The life of this catalyst is about 100 days if the temperature does not exceed 500°C. The ammonia is liquefied and separated as liquid in receivers. The reacting gases are recirculated, and the yield is reported to be from 20 to 30 per cent.

World capacity for the production of synthetic ammonia, by various processes (Report No. 114; 1937, page 341)

Process	Total (tons)*	Total (as per cent of world capacity)
Haber-Bosch	1,138,750	35.2
Casale	481,680	14.9
Fauser	355,080	11.0
Claude	303,020	9.4
I.C.I.**	274,450	8.5

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[62] Curtis, H. A.: *Fixed Nitrogen*, New York, Reinhold Publishing Corp., (1932).

[63] Woodruff: *Ind. Eng. Chem.*, **19**, 1149 (1927).

[64] Larson: U. S. Patent 1,489,497.

[65] Ernst, Reed, and Edwards: *Ind. Eng. Chem.*, **17**, 775 (1925).

Process	Total (tons)*	Total (as per cent of world capacity)
Mt. Cenis	259,000	8.0
N.E.C.†	210,170	6.5
G.C.C.††	200,000	6.2
American ‡	7,800	0.2
Other ‡‡	1,850	0.1

* In tons of 2000 pounds of nitrogen.

** Process of Imperial Chemical Industries—a modification of the Haber-Bosch process.

† Process of Nitrogen Engineering Corporation.

†† Process of General Chemical Co. (affiliate of Solvay Process Co.).

‡ Process of the Fixed Nitrogen Research Laboratory, U. S. Department of Agriculture.

‡‡ Hecker and Jourdan processes.

See also Cope: *Chem. Eng. News*, **23**, 243 (1945).

Oxidation of Ammonia into Nitric Acid

The oxidation reaction:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O + 215{,}600 \text{ cal.}$$

is not practicable without a catalyst as it would take place above 2000°C only, where the NO would dissociate, and the mixture would be explosive. To overcome this, catalysts, notably platinum, are used. The cooled gases are then oxidized to NO_2 which is absorbed in water, HNO_2 and HNO_3 being formed. The general processes are as follows: [66]

$$2NO + O_2 \rightarrow 2NO_2 \text{ (trimolecular, slow; gases cooled)}$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

The partial reactions in the oxidation of ammonia are as follows: [67]

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[66] Chilton: *Ind. Eng. Chem.*, **32**, 24 (1940).

[67] Partington: *Nature*, **117**, 756 (1926).

	Per cent NH_3 in mixture
1. $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O + 302{,}000$ cal.	21.87
2. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O + 215{,}600$ cal.	14.38
3. $2NH_3 + 3O_2 \rightarrow 2HNO_2 + 2H_2O$	12.28
4. $4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O$	10.72
5. $NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$	9.50

According to Partington,[67] the yields from reactions III, IV, V, are almost equally good, although III appears to be best. In practice, an ammonia content, in the air mixture, of 10 volume per cent or less is used.[68]

The oxidation of ammonia, in contact with platinum, is quite substantial at 160°C and a time of contact of 5.10^{-3} seconds, and the oxidation is almost complete at 400°C.[69] Between 500 and 1300°C the possible NO-yield, when the rate of flow is suitable, is about 90 per cent.

The optimum contact period, between the reacting gases and the platinum gauze, decreases as the temperature is raised:[17, 69]

Temperature	Contact period, seconds
Red heat	$<10^{-2}$
845°C	1. 8×10^{-4} (1 atm.) 2. 2×10^{-4} (5 atm.)
700–900°C	10^{-4}–10^{-5}
Very high	$<10^{-6}$

Bodenstein[70, 71, 72] gives the following account for the reaction mechanism of the oxidation of ammonia in the presence of a platinum catalyst at 1140, 1250, and 1350°C:

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[68] Parsons: *Ind. Eng. Chem.*, **19**, 789 (1927).

[69] Andrussov: *Z. anorg. allgem. Chem.*, **39**, 331 (1926); *ibid.*, **40**, 168 (1927).

[70] Bodenstein: *Z. Elektrochem.*, **41**, 466 (1935).

[71] Bodenstein: *Ibid.*, **47**, 501 (1941).

[72] Bodenstein and Buttner: *Congr. intern. quim. pura aplicada, Madrid*, **3**, 475 (1934).

$$NH_3 + O \rightarrow NH_2OH$$

$$NH_2OH + O_2 \rightarrow HNO_2 + H_2O$$

At low temperatures (500°C), large excess of oxygen, and oxide catalysts:

$$NH_2OH + O \rightarrow HNO + H_2O$$

$$2HNO \rightarrow N_2O + H_2O$$

Nitric acid is formed according to:

$$HNO + O_2 \rightarrow HNO_3$$

$$HNO_2 + O \rightarrow HNO_3$$

Free nitrogen is formed according to:

$$HNO_2 + NH_3 \rightarrow 2H_2O + N_2 \text{ (at higher temperatures)}$$

$$HNO + NH_2OH \rightarrow 2H_2O + N_2 \text{ (at lower temperatures)}$$

These reactions would lead to the assumption that the oxidation of ammonia proceeds homogeneously as well as heterogeneously. Experiments, on oxidation of ammonia between 550 and 800°C, with varied distance between the platinum screens used as catalyst point toward this assumption. From these experiments, also the conclusion may be drawn that the catalytic oxidation of ammonia is a hetero-homogeneous reaction at this rather low temperature.[73]

The importance of the rate of flow of the mixed gases is judged by the fact that free nitrogen may be formed from the ammonia according to:[74]

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

which is due to: $2NO \rightleftarrows N_2 + O_2$, caused by too long contact of NO with the catalyst. If the rate of flow of NH_3 is too high, loss occurs according to:

$$NH_3 + HNO_2 \rightarrow N_2 + 2H_2O$$

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[73] Vainshtein and Polyakov: *J. Phys. Chem. (U.S.S.R.)*, **15**, 164 (1941); *Chem. Abstracts*, **36**, 6401 (1942).

[74] Webb: *J. Soc. Chem. Ind.*, **50**, 128T, (1931).

The actual reactions involved in oxidation of ammonia are very complex and vary very much with the reaction conditions.

Platinum was originally used as a catalyst (by Ostwald[75]) in the form of a foil which had a rather low conversion capacity. Later and at present, a platinum gauze is used, which is standardized to give optimum conversion, i.e., conversion of about 90 per cent of the ammonia. The activity of the gauze is low at the commencement of the reaction, but increases to a maximum in a day or so. Some platinum is lost during the operation, especially at high temperatures (above 900°C, Fauser[58, 59, 60]). The loss of platinum is from about 0.1 to 0.2 grams per ton of nitrogen. Gauzes of 90 per cent Pt and 10 per cent Rh resist high temperature better than those of pure Pt.[76] (See page 169.)

Catalyst poisons, for ammonia oxidation, are dust, tar, oil, AsH_3, PH_3, H_2S, C_2H_2, SiH_4, H_2SiF_6, halogens, selenium compounds, etc.[17, 53, 62] The common occurrence in the air of some of these substances necessitates strict control of the purity of the reacting gases.

Many catalysts have been suggested for this reaction. Rhodium is very active, the optimum conversion temperature for 0.1% Rh asbestos being from 600 to 635°C. Ru and Os are too readily oxidized. Oxidation of ammonia, in contact with Pd or Ir, gives nitrogen oxides; high yields with Pd, and low yields with Ir.[17] Platinum, containing 3 per cent tungsten, is claimed to be twice as active as platinum gauze at 750°C.[17] Numerous oxides and other chemical compounds have been tried out for oxidation of ammonia to nitrogen oxides and nitric acid: ThO_2;[77] $Fe_2O_3 + Bi_2O_3$;[49] $Co_2O_3 + Al_2O_3$;[78] etc.

As stated above, the oxidation of ammonia is a very rapid process. The nitric oxide formed is conducted through heat exchangers, where it is cooled and then to absorption towers, where it is oxidized, by a comparatively slow process, to nitrogen dioxide (at about atmospheric temperature):

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[75] Ostwald: British Patent 698 (1902).

[76] Handforth and Tilley: *Ind. Eng. Chem.*, 26, 1287 (1934).

[77] Frank and Caro: German Patent 224,329 (1907).

[78] Fogler: U. S. Patent 1,936,936 (1933).

$$2NO + O_2 \rightleftarrows 2NO_2$$

The dioxide is absorbed in the water in the absorption towers:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

The NO is reoxidized. The strength of the tower acid is about 50–55 per cent HNO_3.

In dilute solutions of nitric acid, up to 30 per cent, there is an equilibrium of $HNO_3:HNO_2$ averaging 9:1:

$$3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O$$

If the temperature rises, the equilibrium is shifted toward the right; if the pressure of NO increases, the equilibrium is shifted toward the left.[79, 80, 81, 82] The velocity of this reaction is claimed not to be influenced catalytically, although sugars and glycerol enhance the decomposition of HNO_2 very strongly.[83, 84] Sulfuric acid and sulfates, especially sodium sulfate, retard both the forma- and the decomposition of HNO_2, the sulfate ion, SO_4^{--}, being the retarding agent. Its retarding action is considered to be due to formation of the bisulfate ion, HSO_4.[85, 86]

The acid, from the absorption towers, containing some 50 per cent HNO_3 is concentrated by adding 66° Bé sulfuric acid and distilling off the HNO_3, which, in this way, can be obtained at a strength of 95–98 per cent. The H_2SO_4 retains the water from the tower acid and is diluted to about 75 per cent. Processes have also been developed for concentration using pressure and cooling to remove the moisture from the acid in the converter.[59, 87, 88] The

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[79] Bode: *Z. anorg. allgem. Chem.*, **195**, 195 (1931).

[80] Briner and Durand: *Compt. rend.*, **155**, 1497 (1912).

[81] Klemenc and Hayek: *Z. anorg. allgem. Chem.*, **186**, 181 (1930).

[82] Klemenc and Klima: *Ibid.*, **179**, 401 (1929).

[83] Dhar: *Z. anorg. allgem. Chem.*, **144**, 296 (1925).

[84] Klemenc and Pollack: *J. Phys. Chem.*, **101**, 171 (1922).

[85] Abell and Schmidt: *Z. phys. Chem.* **134**, 290 (1928).

[86] Abell, Schmidt, and Babad: *Z. phys. Chem.*, **136**, 141 (1928).

[87] *Lonza Elektrizitätswerke u. chem. Fabriken A.G.* (Switzerland): British Patent 418,916 (1934).

[88] Taylor: U. S. Patent 1,840,063 (1932).

drawback exists that the oxidation of ammonia is less effective under increased pressure,[80] and cooling and pressure plants are comparatively expensive.

If the hydrogen, used in manufacturing ammonia, is derived from water gas or generator gas, the CO_2 formed can be used to fix the NH_3:

$$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$$

which, in turn, can be brought to react with $CaSO_4$, and in actual manufacture, natural gypsum or anhydrite is used:

$$(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3$$

Hydrogen cyanide, HCN, is formed by catalytic reaction between CO and NH_3:

$$CO + NH_3 \rightarrow HCN + H_2O$$

As catalyst, oxides of aluminum or cerium have been studied, the actual mechanism being at 500–700°C:[89, 90]

$$2CO + NH_3 \rightarrow HCN + CO_2 + H_2$$
$$CO_2 + H_2 \rightarrow CO + H_2O$$

The following side reaction is indicated:

$$2CO \rightarrow C + CO_2$$
$$C + NH_3 \rightarrow HCN + H_2$$

One part of ammonia and 9.4 parts of CO were passed over a catalyst prepared by adding concentrated ammonia to a solution of $Al(NO_3)_2$, and treating the dried $Al(OH)_3 \cdot aq.$ with a solution of a zirconium salt.[91]

By passing equal volumes of NH_3 and $CH_2{=}CH_2$ at 700°C over pure alumina or quartz + alumina, HCN is obtained.[92] CH_4 may also be used in this synthesis.[93, 94] NH_3 may also be passed

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[89] Bredig, Eloed, and Muller: *Z. Elektrochem.*, **36**, 1003 (1930).

[90] Bredig, Eloed, and Koertnem: *Ibid.*, **36**, 1007 (1930).

[91] Fuchs and Verbeck: *Ind. Eng. Chem.*, **27**, 410 (1935).

[92] Bredig, Eloed, and Demme: *Z. Electrochem.*, **36**, 991, 1001 (1930).

[93] Andrussov: *Z. angew. Chem.*, **48**, 593 (1935).

[94] Fulton: U. S. Patent 1,872,923 (1932).

over diatomaceous earth at 1100 to 1150°C, after being led through toluene at 50–55°C (7:1 ratio), or benzene at 28°C (6:1 ratio).[94] A mixture of CO and NH_3, passed over carbides of Fe, Ni, or CO at 450°C, also yields HCN.[95]

Hydrogen cyanide is obtained by catalytic dehydration of formamide:

$$HCO{\cdot}NH_2 \rightarrow HCN + H_2O$$

If the vapors of $HCO{\cdot}NH_2$ are dehydrated at reduced pressure over artificial zeolites, $CaCl_2$, or alkali carbonates at 400–450°C, full conversion is obtained.[96] Other catalysts used are Fe, Mn, Ni, Al, or Cu; [97] and MnO.[98]

Moissan,[99] in his classic work on carbides, showed that pure calcium carbide does not absorb nitrogen below 1200°C, whereas Frank and Caro [77, 100, 101] showed that technical carbides, containing metallic chlorides as impurities, absorb nitrogen rapidly below 1100°C.[102] This discovery led to the present technical process in which up to 10 per cent calcium chloride (on the carbide) is added to the charge. The reaction proceeds at about 800°C:

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

At 1200°C and above, the cyanide is formed:

$$CaC_2 + N_2 \rightarrow Ca(CN)_2$$

It is possible that the calcium chloride, at least in part, acts as a flux. The reaction is exothermic and requires heat only in order to start.

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[95] Johnson: British Patent 300,369 (1928) (for I. G. Farbenindustrie A.-G.).

[96] Johnson: British Patent 279,530 (1926).

[97] British Patent 269,166 (1927).

[98] Larson: British Patent 470,406 (1937).

[99] Moissan: *Compt. rend.*, **118**, 501 (1894); *Bull. soc. chim.*, **11**, 1002 (1894).

[100] Caro: *Z. angew. Chem.*, **19**, 1569 (1906); *ibid.*, **22**, 1178 (1909).

[101] Frank: *Ibid.*, **19**, 835 (1906).

[102] Landis: *Chem. Met. Eng.*, **12**, 265 (1914); *ibid.*, **13**, 213 (1915); *ibid.*, **22**, 265 (1920).

Iron powder serves as a catalyst in the fixation of nitrogen by a heated mixture of Na_2CO_3 and coke for preparation of NaCN:[103]

$$Na_2CO_3 + 4C + N_2 \rightarrow 2NaCN + 3CO$$

Barium carbonate may also be used, and the oxides of Ti, Mo, Cr, and Mn serve as catalysts:

$$BaO + 3C + N_2 \rightarrow Ba(CN)_2 + CO$$

Hydrazine, $NH_2{\cdot}NH_2$, is formed by the action of NaClO on NH_3:[104]

$$NH_2Cl + NH_3 + NaOH \rightarrow NH_2{\cdot}NH_2 + NaCl + H_2O$$

Salts of Cu, Fe, Ni, Pb, Hg, and especially Co cause considerable decrease in yield, this action being ascribed to the reaction:[104, 105]

$$3NH_2Cl + 3NaOH \rightarrow N_2 + 3NaCl + NH_3 + 3H_2O$$

Containers of these metals also act as negative catalysts for this reaction. This negative catalysis is counteracted by formaldehyde, which, in alkaline solution, condenses to sugar; consequently, sucrose, levulose, glucose, lactose, dextrine, starch, and glycerin also counteract the above negative catalysts.

In soils, nitrogen is fixed by being first hydrated (enzymatically by microorganisms), and afterwards reduced, complex iron compounds acting as catalysts:[106]

$$N_2 + 2H_2O \rightarrow NHOH{\cdot}NHOH$$
$$NHOH{\cdot}NHOH + H_2 \rightarrow 2NH_2OH$$

The NH_2OH is either reduced to NH_3 or it forms oximes with $=CO$ groups.

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[103] Muhlert, F.: *Die Industric der Ammoniak und Cyanverbindugen*, Leipzig, 1915.

[104] Thiele: *Liebigs Ann. Chem.*, **273**, 160 (1893).

[105] Raschig: *Ber.*, **40**, 4587 (1907).

[106] Blom: *Zentr. Bakt. Parasitenk.*, 11, **84**, 60 (1931).

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2. Acetylene derivatives

During World War I, a group of chemists, at Shawinigan Falls, Canada, pioneered in the manufacture of acetylene chemicals from calcium carbide in order to supply acetone.[2] This industry has since then [1] grown to considerable dimensions. A brief outline of the production of acetylene chemicals, as carried out in 1933, is given by Cadenhead.[2]

The operations, for making acetylene derivatives from calcium carbide, are divided in four major groups:

(1) Hydration of acetylene (acetaldehyde process)
(2) Oxidation of acetaldehyde to acetic acid
(3) Distillation of the crude acetaldehyde and of the crude acetic acid
(4) Production of solvents and other compounds from the acetylene

For hydration of the acetylene, the gas, from the generators, of 99.5–99.7 per cent purity, is forced by a Nash Hytor blower through a reaction kettle in which it is converted into acetaldehyde. The kettle is maintained automatically at a temperature of 80°C, and the aldehyde formed then passed through a number of water and brine condensers where the bulk of the aldehyde condenses.

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[1] Moissan, H.: *The Electric Furnace*, London, Edward Arnold, 1904.

[2] Cadenhead: *Chem. Met. Eng.*, **40**, 184 (1933).

Finally, the aldehyde passes through a plate and boiling cap scrubbing column which reduces the aldehyde concentration in the gas to about four per cent by volume. The acetylene, from the scrubber, is used over again after being mixed with a fresh supply of acetylene from the feed main.

The reaction kettle, for hydrating the acetylene, is made of Duriron and is of 4 feet 6 inches diameter, and 23 feet height. Mercury salts, suspended in dilute sulfuric acid, act as catalyst. This catalyst has to be renewed from time to time and is then drawn from the bottom of the kettle mainly in the form of metallic mercury which is worked up again to the original mercury salt catalyst.

As the hydration reaction is exothermic, it must be regulated in order to control the temperature, which is accomplished by gradual addition of the catalyst.

The acetaldehyde, from the condensers and the scrubber, is collected in tanks as a twenty per cent solution, which is kept cool by means of brine coils.

The crude acetaldehyde is distilled on continuous aldehyde stills to 99.9 per cent purity. This aldehyde is oxidized in aluminum-lined steel kettles, in the presence of manganese acetate, by blowing air into the kettles at 60°C and 65 lb pressure. After 12 to 15 hours, the oxidation is complete and crude acetic acid or acetic acid of 96 to 97 per cent purity is obtained. This acid is purified on acetic acid still for producing "B.P." and "edible" grades of acetic acid.

At Shawinigan, 32 tons of oxygen are required daily for oxidation (1933), i.e., 150 to 160 tons of air. The residual 120 to 130 tons of nitrogen are used to flush out and keep under an atmosphere of nitrogen all equipment containing either acetylene or acetaldehyde, or for purging the acetylene generators, but the bulk of the nitrogen is wasted.

Ethylacetate is made from refined aldehyde by condensation in the presence of aluminum ethylate or aluminum ethoxide. Two molecules of acetaldehyde react to form ethylacetate:

$$2CH_3CHO \rightarrow CH_3\cdot COO\cdot CH_2CH_3$$

this reaction scheme expressing the reaction in part. The conversion is good and the yield high. A small amount of butyleneglycol monoacetate is formed and remains as a residue.

Vinyl acetate is produced by a reaction between acetic acid and acetylene in the presence of a catalyst. This compound is the starting point for the series of polyvinyl resins known as Gelvas, Alvars, Formvars, and Butvars, manufactured by Shawinigan.

Vinyl acetate polymerizes readily especially in summer time, and small amounts of stabilizer have to be added to it before shipments, the acetate and the stabilizer later being separated by a single distillation.

Aldol, $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO$, is the dimer of acetaldehyde and is produced by the action of hydroxyl ions on the aldehyde. Sedol is a source of crotonaldehyde, $CH_3{\cdot}CH{=}CH{\cdot}CHO$, which is formed by dehydration, the water being eliminated from the aldol by distillation at atmospheric pressure:

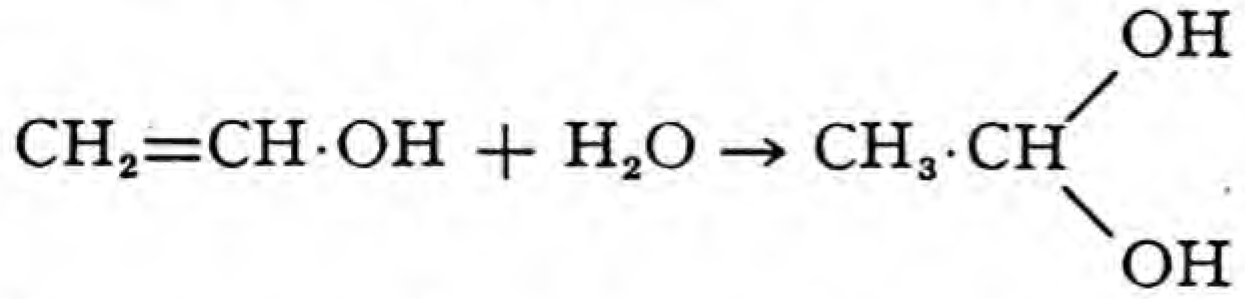
$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO \rightarrow CH_3{\cdot}CH{=}CH{\cdot}CHO + H_2O$$

Croton aldehyde, in turn, can be converted into butyl aldehyde by hydrogenation over various catalysts, and the butyl aldehyde can be further hydrogenated to form butyl alcohol, or oxidized to butyric acid. Crotonic acid is made by blowing air or oxygen through the aldehyde, and from the acid various esters can be made which are important as solvents.

Paraldehyde is produced by the action of hydrogen ions on acetaldehyde.

The reaction mechanism for hydration of acetylene, in the presence of mercury salts, in dilute sulfuric acid, is considered to be as follows:[3, 4]

$$CH{\equiv}CH + HOH \rightarrow CH_2{=}CH{\cdot}OH + \text{heat}$$



$$CH_2{=}CH{\cdot}OH + H_2O \rightarrow CH_3{\cdot}CH\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}$$

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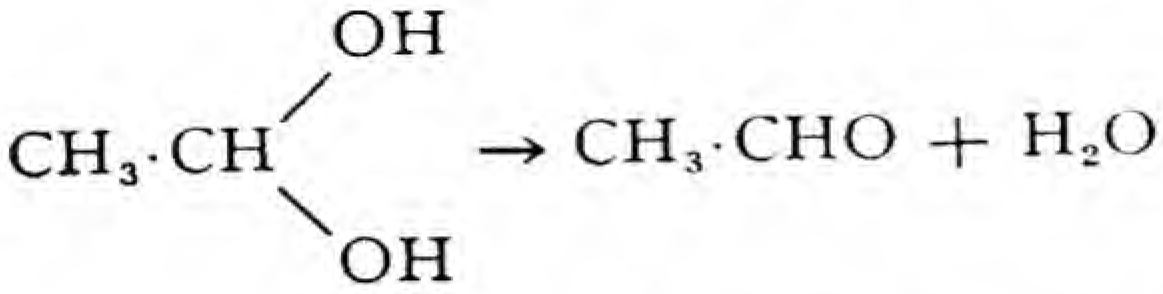
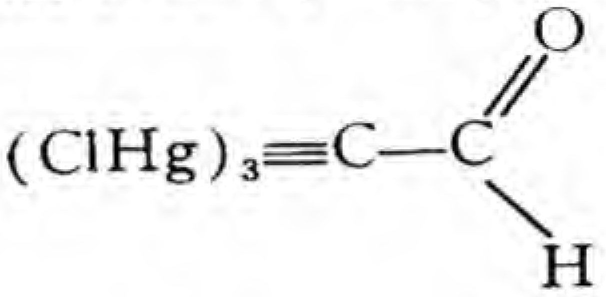
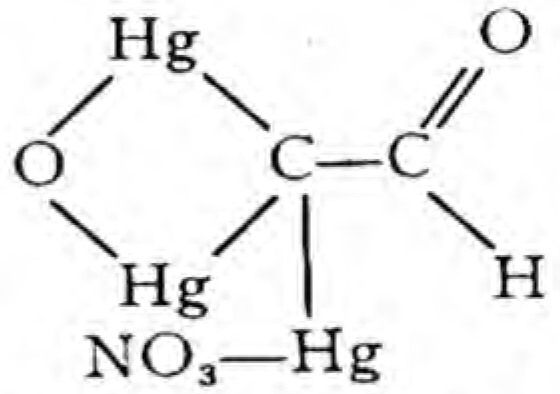
[3] Bone and Andrews: *J. Chem. Soc.*, **87**, 1232 (1905).

[4] Vogel, J. H., and A. Schultze: *Carbid als Ausgangmaterial für Produkte der chemischen Industrie,* Leipzig, Otto Spamer, 1924.



$$CH_3 \cdot CH(OH)_2 \rightarrow CH_3 \cdot CHO + H_2O$$

It is postulated that acetylene combines with the mercury salts to form intermediary compounds:[5, 6, 7]

Mercury salt	Intermediary compound
$HgCl_2$	
$Hg(NO_3)_2$	
$HgCl_2$	$CH \equiv CH \cdot HgCl_2$ or $ClHg \cdot CH = CHCl$

Acetylene may also be converted to acetaldehyde by hydration in the vapor phase in contact with various catalysts: Fe_2O_3, MoO_3, ZnO, etc.:[8, 9, 10]

$$C_2H_2 + H_2O \rightarrow CH_3 \cdot CHO$$

In the oxidation of acetaldehyde in solution, peracetic acid is present in substantial concentration in the reaction liquids, and especially so when chromium oxide, cobalt acetate, iron oxide, or manganese dioxide are used as catalyst:[11]

$$CH_3CHO + O_2 \rightarrow CH_3CO \cdot O \cdot OH$$

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[5] Biltz and Mumm: *Ber.*, **37**, 4417 (1904); **38**, 133 (1905).

[6] Chapman and Jenkins: *J. Soc. Chem. Ind.*, **38**, 655 (1919).

[7] Rooney: *Chem. Met. Eng.*, **22**, 847 (1922).

[8] Rhenania Verein chemischer Fabriken: German Patents 365,285 (1913), 369,515 and 379,596 (1916).

[9] Deutsche Gold- und Silberscheideanstalt A.-G.: German Patent 334,357 (1916).

[10] Ipatieff and Schaad: U. S. Patent 2,253,034 (1941).

[11] German Patent 305,550 (1914).

The peracetic acid is unstable (explosive), and the function of the catalyst is to decompose this compound:[12]

$$CH_3CO{\cdot}O{\cdot}OH + MnO_2 \rightarrow CH_3COOH + MnO_3 \text{ or intermediate oxides}$$

$$MnO_3 \text{ or intermediate oxides} + CH_3CHO \rightarrow CH_3COOH + MnO_2$$

Various chlorinated compounds are made from acetylene. Thus, symmetrical tetrachloroethane is prepared from acetylene using antimony pentachloride as a catalyst:[15]

$$CH{\equiv}CH + SbCl_5 \rightarrow CH{\equiv}CH{\cdot}SbCl_5$$

By heating, the following reaction takes place:

$$CH{\equiv}CH{\cdot}SbCl_5 + SbCl_5 \rightarrow CHCl_2{\cdot}CHCl_2 + 2SbCl_3$$

In the industrial process, acetylene and chlorine are separately brought into antimony pentachloride in order to avoid explosion. The intermediate compounds $SbCl_5{\cdot}C_2H_2$ and $SbCl_5{\cdot}2C_2H_2$ are formed, which react with chlorine to give tetrachloroethane, and the $SbCl_5$ is regenerated and used over again, as a true catalyst.

Hexachloroethane is made by exhaustive chlorination of the tetrachloride with $AlCl_3$ as catalyst:

$$C_2H_2Cl_4 + 2Cl_2 \rightarrow C_2Cl_6 + 2HCl$$

A number of condensation products can be made by reacting acetylene, in the presence of the proper catalysts, with ammonia, carbon dioxide, or acetic acid.

In connection with the waste of nitrogen, left over from the air used in the oxidation process, Berthelot's[16] reaction between acetylene and nitrogen in the electric arc or in contact with platinum sponge at 800°C may be of interest, as it offers a method for preparing hydrogen cyanide:

$$C_2H_2 + 2N \rightarrow 2HCN$$

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[12] Riegel, E. R.: *Industrial Chemistry.* New York, Reinhold Publishing Corp., 1937, p. 429.

[15] Berthelot and Jungfleisch: *Liebigs Ann. Chem.,* Suppl., 7, 252 (1870).

[16] Berthelot: *Liebigs Ann. Chem.,* **150, 60** (1869).

The thermodynamical feasibility of this reaction has been discussed by Ewell,[17] and a detailed investigation has been made by Elöd and Nedelmann.[17a]

Another interesting possibility is the synthesis of phenol from acetylene (Meyer): [18]

$$3C_2H_2 + H_2O \rightarrow C_6H_5OH + H_2$$

3. Products from carbon oxides and water gas

It is a peculiar fact that organic catalytic reactions are selective in that they follow a definite path of reaction depending on the catalyst used. Thus, Mittasch [1] and Fischer and Tropsch [2] demonstrated how carbon monoxide and hydrogen, according to the catalyst used, yield 1) methane, 2) homologs of methane, 3) methyl alcohol, or 4) homologs of methyl alcohol (Synthols), together with a wide variety of other compounds such as acids, ketones, aldehydes, and esters.

These studies originate from Sabatier's classic studies (1902) on the hydrogenation of carbon monoxide over nickel to methane:[3, 7]

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

The hydrogenation starts between 180 and 200°C and proceeds rapidly at 230 to 250°C, a mixture of the theoretical proportions being converted to almost pure methane.

Later, in 1913, the Badische Anilin-und Soda-Fabrik [4] took out a patent on treating water gas, at about 400°C and under 100 atmospheres pressure, in contact with various catalysts (especially the metals of the iron group with alkalies, zinc, and zinc oxide) to form a mixture of hydrocarbons, alcohols, aldehydes, and ketones. In the twenties, considerable efforts were made to exploit this reaction, the most notable results being obtained by Fischer and Tropsch, whose work is reported below in some detail.

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[17] Ewell: *Ind. Eng. Chem.*, **32**, 153 (1940).

[17a] Elöd and Nedelmann: *Z. Elektrochem.*, 33, 217 (1927).

[18] Meyer: *Ber.*, **45**, 1609 (1912); *ibid.*, **46**, 3183 (1913); *ibid.*, **47**, 2765 (1914); *ibid.*, **50**, 422 (1917); *ibid.*, **53**, 1261 (1920).

[1] Mittasch: *Ber.*, **59**, 29 (1926).

[2] Fischer and Tropsch: *Ibid.*, **59**, 830 (1926).

[3] Sabatier, P., and E. Emmett Reid: *Catalysis in Organic Chemistry. 2nd Ed.*, New York, D. Van Nostrand Company, 1923, p. 393.

[4] Mittasch and Schneider: German Patent 293,787 (1923).

Fischer and Tropsch [5, 6, 7] produced water gas, as free as possible from sulfur compounds and compressed the gas to 150 atmospheres. The gas was passed through a high-pressure apparatus at 400 to 450°C in contact with iron shavings coated with potassium carbonate. Under these conditions when the apparatus was left standing, a liquid was formed in the cooled receiver vessel. This liquid consisted of an aqueous and an oily layer in the proportion of one part oil to two parts aqueous solution. One fifth of the latter consisted of a mixture of aliphatic alcohols, aldehydes, and ketones besides free fatty acids; but the major part of the liquid consisted of "oily" substances. Analyses disclosed the following products resulting from the treatment of water gas in the high-pressure apparatus: [5, 8]

Total amount in the single groups	Identified:	Approximate amount of the identified compounds in per cent of the reaction products of all the groups
10 per cent acids:	Formic	0.1
	Acetic	2.3
	Propionic	2.1
	Isobutyric	1.0
	Higher fatty to C_8	4.5
29 per cent water-soluble alcohols, aldehyde, and ketones	Methyl alcohol	1.5
	Ethyl alcohol	14.5
	Propyl alcohol	
	Acetone	5.2
	Methyl-ethyl-ketone	
11 per cent oils, partly miscible with water		

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[5] Fischer and Tropsch: *Brennstoff-Chem.*, **4**, 276 (1923).

[6] Fischer and Tropsch: *Ber.*, **56**, 2428 (1923).

[7] Fischer: *Brennstoff-Chem.*, **16**, 1 (1935).

[8] Fischer and Tropsch: *Brennstoff-Chem.*, **7**, 97, 299 (1926).

Total amount in the single groups	Identified:	Approximate amount of the identified compounds in per cent of the reaction products of all the groups
48 per cent oil, volatile with steam	Propionic aldehyde	
	Isobutyric aldehyde	
	Diethyl ketone	
	Methyl-n-propyl ketone	
	Higher alcohols up to C_9	15.0
	Ester	2.0
	Hydrocarbons	1.3
2 per cent oil, not volatile with steam		

Since this classic experiment was carried out, the process has been further developed. Later it was established that the water gas, at atmospheric pressure,[7] can be converted into a mixture of liquid and gaseous hydrocarbons containing very little of oxygenated products, in fact in traces only. Iron activated with copper and alkali, or cobalt activated with zinc oxide was used as catalyst. Nickel was first considered purely a hydrogenation catalyst for converting the carbon monoxide to methane, but later, promoted nickel catalysts were made which were suitable for producing liquid hydrocarbons, as well as cobalt.

The gas mixtures were purified from hydrogen sulfide and organic sulfur compounds, and it took nine years to adapt the purification process to operation on a technical scale.

For iron catalysts, a temperature of approximately 250°C is required, and for cobalt 180 to 200°C. If the gas mixture is rich in hydrogen, lower temperatures are required, and if the gas mixture is low in hydrogen, higher temperatures are absolutely necessary. The reaction mechanisms, for the two catalysts mentioned, are suggested to be as follows:

1. Iron catalyst at about 250°C:

$$H_2 + 2CO + Fe_3C \rightarrow Fe_3C_2 + H_2 + CO_2 \rightarrow$$
$$Fe_3C + (CH_2) + CO_2$$

2. Cobalt or nickel catalyst below 200°C:

$$2H_2 + CO + Co_3C \rightarrow Co_3C_2 + H_2 + H_2O \rightarrow$$
$$Co_3C + (CH_2) + H_2O$$

The operation conditions have substantial influence on the products resulting from this synthesis, the relations being as follows:

1. Increasing pressure → Synthol
2. Increasing hydrogen content → methane (decrease of temperature necessary) increasing saturation
3. Decreasing hydrogen content → olefins
4. Increasing temperature → methane and carbon
5. Catalyst metals in the series Fe, Co, Ni → increasing saturation, i.e., less olefins
6. Presence of CO_2 → without influence, acts as inert admixture only
7. Increasing working age of the catalyst → relatively more benzine, less oil

The benzine obtained by this process was named Kogasin. It consists of paraffin hydrocarbons and a small amount of olefin hydrocarbons, both predominatingly with unbranched chains and very different boiling points. As already mentioned, oxygenated compounds are present in traces only.

Raw materials for these processes are: Water gas, generator gas, high-oven gas, blast furnace gas, a mixture of blast furnace and coal gas (as for lighting), or blast furnace gas and hydrogen.[7]

Theoretically, one cubic meter of water gas yields approximately 190 grams of hydrocarbons. To obtain full yield, in practice, recycling of the gas mixture over the contact, until all of the carbon monoxide is used up, is required. Furthermore, the gas mixture must be free from sulfur compounds (H_2S and organic; not more than 0.2 grams per 100 m^2) in order to prevent poisoning of the catalyst, and the temperature must be accurately controlled, as too high temperature inevitably leads to formation of methane.

Production of synthesis gases. (1) They may be obtained from coke. In most cases, it is endeavored to obtain a gas mixture which contains carbon monoxide and hydrogen in a ratio of 1:2. Consequently, the gasification of coke, at low temperature and higher addition of steam, is of importance in this connection, as it permits the formation of a gas mixture which to two parts of carbon monoxide contains four parts of hydrogen and one part of carbon dioxide. For formation of Kogasin, carbon monoxide and hydrogen are here in the right ratio, and under proper working conditions, the carbon dioxide is not converted but acts merely as a diluent.

It is outside the scope of this book to go into details of the different installations, but it should be mentioned that Fischer calls attention to the fact that where cheap hydroelectric power is at hand, production of water gas with steam, in electric ovens, is feasible, a condition which is of considerable interest for this northern continent with its abundance of hydroelectric power. Fischer also suggests the use of lignite half-coke (Braunkohlenhalbkoks) if it can be gasified in a suitable converter. (2) Other gases from which Kogasin may be made are tabulated by Fischer as follows:

A. Coke oven gas:

1. Coke oven gas, $CO:H_2$ as 1:10 instead of 1:2
2. Coke oven gas mixed with generator gas or blast furnace gas; N_2-ballast
3. Coke oven gas converted catalytically with steam. $CH_4 + H_2O \rightarrow CO + 3H_2$
4. Coke oven gas converted catalytically according to: $CH_4 + CO_2 = 2CO + 2H_2$
5. Coke oven gas mixed with water gas
6. Coke oven gas converted with steam and mixed with water gas
7. Adding coke oven gas to the steam in the water gas process
8. Coke oven gas converted with steam and mixed with a gas, which is made from coke, steam and oxygen

B. Methane (natural gas):

9. Methane converted with water
10. Methane converted with carbon dioxide.
11. Methane converted with $CO_2 + H_2O$, i.e., formation of $CO + H_2$

C. Carbon dioxide:

12. Reduction of CO_2 on copper contact to CO, and further on cobalt with electrolytic hydrogen to benzine
13. Reduction of CO_2, on coke electrically heated to a high temperature, to CO and further, with electrolytic hydrogen, to benzine

Natural gas (methane), converted with steam or with CO, or, what is better, mixed with both, can give a gas mixture of $CO:H_2=1:2$. Further, CO_2 from terrestric sources can be converted to gasoline by reducing it to CO over copper contacts, and then with electrolytic hydrogen to gasoline. Actually, all that is fundamentally required for this purpose is a cheap source of power.

An exampie of the products, obtained in benzine synthesis from a gas mixture containing about 29 per cent CO and 58 per cent H and converted over a cobalt contact, is as follows:

Product	Boiling point limits °C	Quantity in weight per cent	Olefin content in volume per cent
Gasol	<30*	4	50
Gasoline	30–200	62	30
Oil	>200	23	10
Solid paraffin wax from the oil	m.p. 50	7	
Hard-wax from the contact (extracted)	m.p. 70–80 or more	4	

* Gasol (ethane, propane, and part of the butane; the corresponding olefins, ethylene, propylene, and butylene, were not present in substantial quantities).

The products obtained are water-clear and require only to be freed from traces of organic acids and then to be fractionated. For a gas, containing about 29 per cent carbon monoxide and 58 per cent hydrogen, the average yield of liquid hydrocarbons, per cubic meter gas, is between 100 and 120 grams by one pass over the catalyst. The theoretical yield is 180 grams. It is, of course, likely that higher yields are obtained by now, and those were anticipated at the time this reference was written. It should be noted that the formation of methane, under the working conditions referred to, was practically suppressed.

The catalysts used in this process have been studied very thoroughly, and much valuable information, theoretical as well as practical, has been obtained. Fischer's own summary (1935) is as described here.

The catalyst metals, which are suited for Kogasin synthesis, i.e., iron, cobalt, and nickel, form carbides of the general formula Me_3C and, although no other carbides of these metals are known to exist, it is assumed that the Kogasin synthesis is due to intermediary formation and decomposition of carbides. It can then be assumed that either the carbide Me_3C is formed which, under the action of the hydrogen, is converted into the metal with formation of the unsaturated radical $=CH_2$; or that the carbide Me_3C is formed right away and then by reacting with the CO is converted into a higher carbide which is converted by the hydrogen to the normal carbide, Me_3C with formation of $=CH_2$.

The pure metals, in finely divided form, give poor conversion and such contacts have a short life. Numerous experiments led to mixed catalysts of lasting activity, which gave high conversion, some examples being as follows:

Catalyst	Yield per m^3 mixed gas	Duration of catalytic activity until a decrease of 80 per cent of initial activity
Iron:		
FeCuMn silica gel 0.4% K_2CO_3, dec.*	about 30–35 grams	8 days
FeCu on kieselguhr, prec.*	about 28 grams	8 days
Nickel:		
NiTh kieselguhr, prec.	about 100 grams	30 days
NiMnAl kieselguhr, prec.	about 105 grams	45 days
Cobalt:		
CoTh kieselguhr, prec.	110 grams	60 days
CoTh kieselguhr, dec.	105 grams	25 days
CoMn kieselguhr, prec.	105 grams	at least 30 days
CoNi alloy lattice Si	85 grams	12 days
CoThCu kieselguhr, prec.	105 grams	60 days

* prec.—precipitated; dec.—decomposed

The additions, to the catalyst metals, are in part of definite chemical action, whereas the supports act physically. For instance, copper facilitates the start of the contact action by decreasing the reduction temperature of the oxides. The addition of copper is beneficial for cobalt and iron only, but is detrimental in the case of nickel. The addition of alkali, e.g., to iron, increases the formation of solid paraffin. Supports, such as kieselguhr, asbestos flour, and silica gel increase the distribution of the contact material, thus providing a larger surface. Additions of thorium and manganese and similar ingredients appear to contort the metal lattice.

The precipitated catalysts were made from the nitrates. The alloy catalyst was prepared from an alloy of cobalt and nickel with silicon, the latter component being leached out by means of soda lye. The cobalt contact, containing copper, had a content of this metal of 2 per cent, and this catalyst could be reduced at much lower temperatures than those not containing copper.

Several hundred catalysts were investigated as to their specificity and life. The latter test is very slow, it takes eight weeks. Although, to be sure of the activity of these catalysts, there is no substitute for an experiment up to eight weeks, indications as to the activity can be obtained by determining the apparent density, the heat evolved when the contact mass is moistened with benzene, or the content of reduced metal. Indication as to the quality of the catalyst may also be had by a short run, measuring the contraction of the gas at the lowest temperature, or by using an excess of gas mixture over the catalyst.

However well prepared the catalysts may be, their activity gradually diminishes on account of poisoning by sulfur and sintering which causes increase in the size of the catalyst particles. Penetration of paraffin wax of high melting point also contributes to the decrease of activity with time, although it is assumed that this penetration can go very far before it is totally detrimental.

The catalyst is readily regenerated. The wax is extracted, and the residue dissolved, filtered, precipitated and activated again. By this extraction, from 100 to 150 per cent, on the weight of the catalyst, of paraffin wax of melting points from 70 to 100°C, or higher, is obtained. This paraffin wax is said to be used for making synthetic fatty acids and electric insulators.[10, 11] The regenerated catalyst is as good as the original one, and no material is wasted by the regeneration.

The olefin content is of interest because it renders possible the production of alcohols and esters by hydration methods. Thus, Fischer made amyl alcohols and hexyl alcohols by treating the corresponding olefins with 85 per cent sulfuric acid and decomposing the alkyl sulfuric acid in water.

The olefin content depends considerably on the catalyst used:

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[10] Underwood: *Ind. Eng. Chem.*, **32**, 449 (1940).

[11] Koch and Ibing: *Brennstoff-Chem.*, **16**, 141, 185 (1935).

Major catalyst metal	Volume per cent of olefin in synthetic gasoline by using: Water gas $1\ CO : 1\ H_2$	Mixed gas $1\ CO : 2\ H_2$	Spalt gas $1\ CO : 3\ H_2$
Cobalt	55	35	12
Nickel	35	16	5

Fischer claims that by further modification of the proportions of the gases in the mixtures, it is possible to extend the limits of olefin contents below 5 per cent and above 55 per cent.

It was also found that the higher the boiling point, the lower was the olefin content, this being due to polymerization of the olefins. The polymerized oil fraction constitutes a product suitable for use as a lubricant. Its viscosity can be increased by distilling off some of the lighter fractions.[7]

The Fischer and Tropsch low-pressure process yields three distinct fractions of hydrocarbons which have been further studied by Koch and Ibing:[11]

(I) The gasoline or Kogasin I fraction boiling between 30 and 220°C.
(II) The Diesel oil or Kogasin II fraction boiling between 220 and 350°C.
(III) The wax fraction comprising all paraffin hydrocarbons which are solid at room temperature, i.e., from $C_{17}H_{36}$ (m.p. 22.5°C) upward.

Kogasin II consists of approximately 5 per cent of unsaturated hydrocarbons, the balance being about ⅓ normal hydrocarbons and about ⅔ slightly-branched isoparaffins. The typical hydrocarbons of this fraction are tridecane, tetradecane, pentadecane, and octadecane.

Kogasin II is chlorinated by passing chlorine through the oil under cooling until it contains up to six chlorine atoms in the molecule, which is considered to have a molecular weight of 200. The product consists of a mixture of different molecules and this molecular weight is an average one. This process is based on the fact that chlorine reacts at room temperature with paraffins from decane to octadecane forming alkyl chlorides. The chlorine is bound quite strongly, even the heavily chlorinated compounds being practically stable up to 200°C. The specific gravity of the chlorinated normal paraffins from dodecane to pentadecane is as follows:

Number of chlorine atoms in the hydrocarbon molecule	Approximate specific gravity
1	0.85–0.87
2	0.95–0.99
3	1.05–1.08
4	1.12–1.15
5	1.20–1.24

Koch and Ibing[11] studied the condensation of these alkyl chlorides by activated aluminum, and also their condensation with aromatic hydrocarbons, in the presence of aluminum chloride, in both cases lubricating oils being obtained.

A potential source of raw material, for the Fischer-Tropsch process on the North American continent, is natural gas. It can be converted, as far as methane is concerned, as follows:[10]

$$\text{I.}\quad 3CH_4 + CO_2 + 2H_2O \rightarrow 4CO + 8H_2, \text{ or}$$

$$\text{II.}\quad 2CH_4 + O_2 \rightarrow 2CO + 4H_2$$

Reaction (I) is carried out at 760°C in the presence of a nickel catalyst.

In discussing this problem, Egloff[12] states that U.S.A. produces over 2.6 trillion cubic feet of natural gas, and that this gas contains over 90 per cent of methane which can be converted into carbon monoxide and hydrogen.

In Germany, the Fischer-Tropsch process has been developed to produce oil from carbon monoxide and hydrogen at a rate of about 15,000,000 barrels annually. As this process yields saturated hydrocarbons from methane and up, unsaturated hydrocarbons, gasoline, Diesel oil, and waxes, its potentialities are enormous.

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[12] Egloff: *Science*, **96**, 527 (1942).

GENERAL REFERENCES

(a) Franz Fischer and R. Lessing: *The Conversion of Coal into Oils*, London, Ernest Benn Ltd., 1925; (b) Patart: *Compt. rend.*, **179**, 1330 (1924), *Chimie & Industrie*, **13**, 179 (1925); (c) Morgan et al.: *J. Soc. Chem. Ind.*, **47**, 1175 (1928); *ibid.*, **51**, 1T (1932); (d) Morgan: *Proc. Roy. Soc. (London)*, **A127**, 246 (1930); (e) Taylor et al: *J. Am. Chem. Soc.*, **49**, 2468 (1927); *ibid.*, **53**, 2168 (1931); (f) Frolich et al.: *Ind. Eng. Chem.*, **20**, 287 (1928); (g) Kothrock: Canadian Patent 362,016 (1936); Craxford: *Trans. Faraday Soc.*, **35**, 946 (1939); Herington and Woodworth: *Ibid.*, **35**, 958 (1939).

4. Natural gas

Where natural gas is accessible in abundance, it offers a source of inexpensive starting material for making a considerable number of chemicals by catalytic and other chemical processes. The exploitation of natural gas for making chemicals, therefore, has caught the imagination of petroleum and other chemists, and indeed some very worth-while results have ensued.[1, 2, 3, 4]

Adams,[6] in a discussion of the future of the natural gas industry, states that new developments on natural gas will be concerned with conversion of hydrocarbons into liquid fuels with characteristics superior to those of natural or cracked liquid fuels and with the development of other products such as general organic chemicals.

Since the gas constituents can be readily converted into unsaturated and oxygenated products and also lend themselves to chlorination, fluorination, sulfonation, and other conversions, the potentialities for making chemicals from natural gas are very substantial. The processes, involved in these conversions, are discussed throughout this text and need not be repeated here.

Partial oxidation of natural gas, especially methane, for production of formaldehyde, has been discussed recently by Levey,[5] who suggests to use somewhat less than the calculated amount of air and admit it, as the reaction proceeds, at intermediate points prior to recycling. The best reaction temperature appears to be between

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[1] Egloff: *Science*, **96**, 502, 527 (1942).

[2] Cambron: *Can. Chem. and Met.* (1937).

[3] Storch and Golden: *Ind. Eng. Chem.*, **25**, 768 (1933).

[4] Montagnes: *Chem. Met. Eng.*, **50**, 98 (1943).

[5] Levey: *Chemical Industries*, February, 1942, p. 204.

[6] Adams: *Ind. Eng. Chem., News Edition*, **21**, 964 (1943).

350 and 600°C, the initial pressure being about atmospheric and, in some processes, reaching as high as 250 atmospheres. This oxidation is not essentially catalytic, but it is greatly improved by catalysts. Nitric oxides, phosphorus pentoxide, dimethyl or diethyl ether, oxides of metals, variable oxides, and metals (Mo, V, Co, Ag, Cu, Fe, Al, Cr, Zn, Pt and Pd) are catalysts for this process. Recycling is required as only a fraction of a per cent up to ten per cent formaldehyde is formed per pass. At the same time, methyl alcohol is formed, usually more than formaldehyde, and it can be oxidized to formaldehyde in a special unit.

Jones, Allison and Meighan[7] chlorinated natural gas, containing 98.5 per cent methane, 10.1 per cent ethane, and 0.4 per cent nitrogen. The chlorination, at about 400°C, yielded a distillate of a specific gravity of 1.6, the lower fraction being carbon tetrachloride and the higher fractions a mixture of carbon tetrachloride, hexachlorethane and other chlorinated products. The conversion yield was 90 per cent or better, based on the gas used. It was observed that a small amount of moisture in the gas tended to promote the reaction. For producing CCl_4, activated charcoal gave the larger yields, whereas this catalyst was not suitable for production of CH_3Cl, this latter reaction being catalyzed by coke impregnated with Fe, Ni, Pt, Zn, or Pb. Ethane was chlorinated in preference to methane.

GENERAL REFERENCE

Wiezevich and Frolich: *Ind. Eng. Chem.*, **26**, 267 (1934).

5. Production of alcohols

In the section on hydrogenation of carbon monoxide, it was noted that alcohols and other oxygenated products result when carbon monoxide and hydrogen are compressed over an alkalized iron catalyst.[1, 2] Synthetic methyl acohol, in fact, appeared on the world market right after World War I, and plants for producing this alcohol were erected in the twenties in the United States.[3]

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[7] Jones, Allison, and Meighan: *U. S. Bureau of Mines, Petroleum Technology*, 1921.

[1] Mittasch: U. S. Patents 1,558,559 (1925) and 1,569,775 (1926).

[2] Fischer and Tropsch: *Brennstoff-Chem.*, **4**, 276 (1923).

The production of methyl alcohol from carbon monoxide and hydrogen proceeds according to the reaction:

$$\mathrm{CO} + 2\mathrm{H}_2 \rightleftarrows \mathrm{CH}_3\mathrm{OH} + 27{,}000 \text{ cal.}$$ [5]

The free energy, for this reaction, at 100° C, is —2,500 calories, and at 400°C + 14,300 cal.[4] Consequently, a lower temperature favors this reaction, as does also high pressure.

Fieldner and Brown [6] have tabulated the data of conversion of carbon monoxide to methyl alcohol, carried out by themselves and others, as follows:

Comparative study of values obtained in synthesis of methyl alcohol (Fieldner and Brown)

Experimenter	Original mixture	Space velocity	Temperature °c	Total pressure atm	Conversion of carbon monoxide to methyl alcohol	
					Experimental	calculated by the Nernst approximation formula
1. Audibert and Raineau	$CO+5H_2$	5000	400	150	22.5	24*
	$CO+2H_2$		400	150	14.66	14.6
2. Lewis and Frolich	$CO+2.7H_2$	625	400	204	26	27.0
3. Brown and Galloway	$CO+2H_2$	7500	400	180	16.8	19.0
	$CO+2H_2$	3000	400	180	19.5	19.0

* Calculation by Fieldner and Brown gives 22.4.

The catalyst should allow conversion at lowest possible temperature and be selective so that no side reactions take place. Zinc oxide was used by Patart.[8] It was found later that zinc oxide with chromium oxide gives better results.[7, 8] Other oxides suggested for this process are $3ZnO + CrO_3$;[9] $CuO + Zn$ (3 mol%);[10] $ZnO + Cr_2O_3$.[11]

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[3] Riegel, E. R.: *Industrial Chemistry*, New York, Reinhold Publishing Corp., 1937, p. 442.

[4] Fenske, M. R.: *Hydrogenation*, Chapter VIII in Groggins' *Unit Processes in Organic Chemistry*, New York, McGraw-Hill Book Company, Inc., 1938, p. 419.

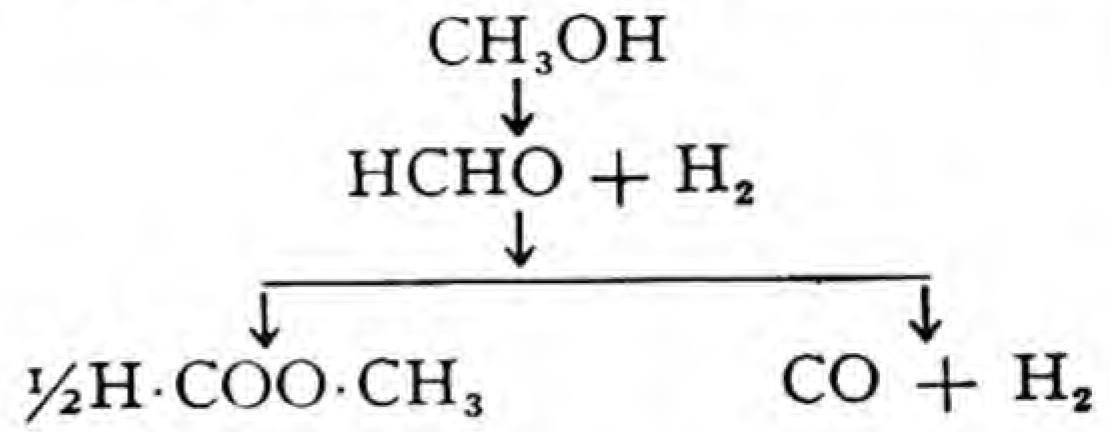
[5] Audibert and Raineau: *Ibid.*, **20**, 1105 (1928).

[6] Fieldner and Brown: *Ind. Eng. Chem.*, **20**, 1110 (1928).

[7] Johnson: British Patents 228,959 and 227,147 (1924), 229,714, 229,715, 231,285, 237,030, 238,319 and 240,955 (1925). (I. G. Farbenindustrie A.-G.)

[8] British Patent 275,345 (1927).

Frolich et al.[10] consider that their method of decomposition of CH_3OH is suitable for study of the activity of catalysts for the synthesis of this alcohol from water gas at high pressure. When pure copper is used, formaldehyde is the principal product, whereas zinc oxide in small amounts favors formation of methyl formate, assumedly due to polymerization of the initially formed formaldehyde. With excess of zinc oxide, carbon monoxide predominates. The reaction schemes for these decompositions are as follows:



Audibert and Raineau[5] conclude that a number of substances, which decompose methyl alcohol at elevated temperature and atmospheric pressure, are capable of catalyzing the synthesis of the alcohol by the reverse reaction using CO and H_2 at high pressure. In this study, it was also found that reduced copper and zinc oxide were the most effective of the methyl alcohol catalysts studied. Manganous oxide and chromium sesquioxide were of considerably lower order, and the remaining oxides were too inactive for consideration to be used singly.

Copper catalysts, prepared from the hydroxide precipitated from a solution of the sulfate or chloride, were entirely inactive. Cuprous and cupric oxides give active catalysts by reduction with hydrogen, when they are prepared by precipitation of the nitrate, or by thermal decomposition of the unstable copper salts of organic acids. Single catalysts are sensitive to heat and are inferior to mixed catalysts.[5]

Ethyl alcohol, $CH_3 \cdot CH_2OH$, can be made by hydrogenation of acetaldehyde using nickel supported on pumice as a catalyst.[12, 14] It is estimated that one ton of alcohol is produced from two tons of calcium carbide.[15]

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[9] Morgan, Taylor, and Hedley: *J. Chem. Soc.*, **47**, 117T (1928).

[10] Frolich, Fenske, and Quiggle: *Ind. Eng. Chem.*, **20**, 694 (1928).

[11] Molstad and Dodge: *Ibid.*, **27**, 134 (1935).

Ethylene is a logical raw material for production of ethyl alcohol, this olefin being present in cracked petroleum and coke oven gas. As it is well known, ethylene, when absorbed at 80 to 85°C in sulfuric acid (95 per cent or less), forms acid ethylsulfate, which, upon hydrolysis, yields ethyl alcohol:

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow CH_3{\cdot}CH_2\ (HSO_4)$$
$$CH_3{\cdot}CH_2(HSO_4) + H_2O \rightarrow CH_3{\cdot}CH_2OH + H_2SO_4$$

In sulfuric acid which is stronger than 95 per cent, diethylsulfate is formed. The ethylene is taken up more efficiently by the sulfuric acid if mineral oil is present. Foam producing agents, olive oil or tetrahydronaphthalene, may also be used with the sulfuric acid.[17] Catalysts may be added to the acid, viz., salts of silver, gold, iron, cobalt, manganese, cerium, chromium, tin and bismuth, or complex salts such as the cyanides.[17] Ethylene may also be adsorbed by H_2SO_4 diluted with a solution of ammonium sulfide in the presence of a complex cyanide, as catalyst, the alcohol being distilled off after treatment with ammonium hydroxide. In this process, ammonium sulfate is obtained as a by-product.

The logical method for making ethyl alcohol from ethylene would be to hydrate the ethylene with steam in vapor phase over a suitable catalyst. It appears that catalysts for this reaction must be both highly selective and highly active. Up to this time, catalysts which will effect a total conversion have not been found. Phosphoric acid, phosphates, boric acid, alumina, pumice or charcoal impregnated with sulfuric acid, etc., have been tried as catalysts.[19]

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[12] Sabatier and Senderens: *Compt. rend.*, **137**, 301 (1903).

[14] Armstrong and Hilditch: *Proc. Roy. Soc. (London)*, A **97**, 259 (1920).

[15] Hilditch, T. P., and C. C. Hall: *Catalytic Processes in Applied Chemistry*, London, Chapman and Hall, Ltd., 1937.

[17] Elkington: British Patent 323,748 (1930) (N. V. de Bataafsche Petroleum Maatschappij).

[19] Howk, B. W., and W. A. Lazier: *The Hydration, Dehydration, and Hydrolysis of Organic Compounds*, Twelfth Report of the Committee on Catalysis, National Research Council, New York, John Wiley & Sons, 1940.

The higher olefins may likewise be hydrated to higher alcohols in the presence of a catalyst. Propylene and butylene yield isopropyl alcohol and butyl alcohol, respectively, in the presence of bismuth salts at 170–150°C and 20–40 atmospheres.[20]

As discussed on page 329 and following, a mixture of alcohols results from the interaction of carbon monoxide and hydrogen in the presence of a catalyst at elevated temperature and pressure. Graves[22] investigated a crude higher alcohol mixture obtained by this type of process, the alcohols having boiling points from 85 to 162°C. The following alcohols were found:

1. Primary alcohols:
   n-propanol
   isobutanol
   2-methyl-1-butanol
   2-methyl-1-pentanol
   2,4-dimethyl-1-pentanol
   4-methyl-1-hexanol
2. Secondary alcohols:
   Isopropanol
   3-methyl-2-butanol
   2,4-dimethyl-3-pentanol

Strong evidence was obtained for the presence of the following alcohols:

1. Primary alcohols:
   2,4-dimethyl-1-hexanol
   4- or 5-methyl-1-heptanol
2. Secondary alcohols:
   3-pentanol
   2-pentanol
   2-methyl-3-pentanol

The following conclusions were made for the mechanism of synthesis:

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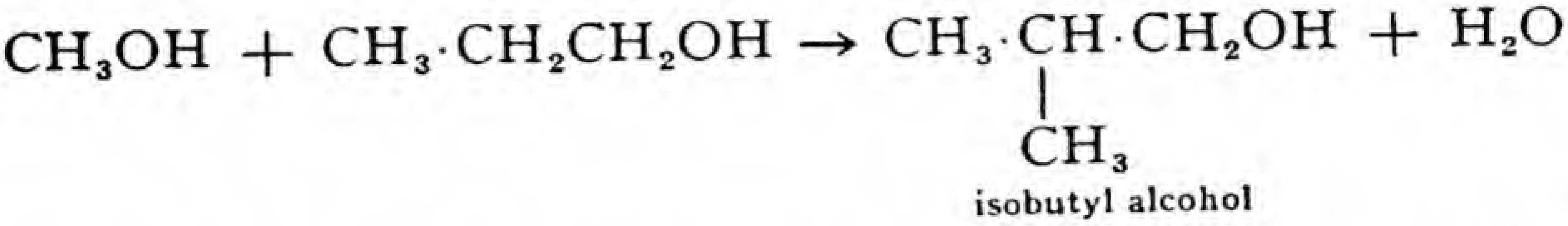
[20] Campmael: British Patent 324,897 (1930). (I. G. Farbenindustrie A.-G.)
[22] Graves: *Ind. Eng. Chem.*, 23, 1381 (1931).

(1) Higher alcohols result from intermolecular dehydration of two lower alcohol molecules:

$$\underset{\text{methyl alcohol}}{CH_3OH + CH_3OH} \rightarrow \underset{\text{ethyl alcohol}}{CH_3CH_2OH} + H_2O$$

$$CH_3OH + CH_3CH_2OH \rightarrow \underset{\text{n-propyl alcohol}}{CH_3CH_2CH_2OH} + H_2O$$



$$CH_3OH + CH_3{\cdot}CH_2CH_2OH \rightarrow \underset{\text{isobutyl alcohol}}{CH_3{\cdot}\underset{\displaystyle CH_3}{\underset{|}{CH}}{\cdot}CH_2OH} + H_2O$$

(2) Dehydration involves removal of hydrogen either from the hydroxylated carbon atom, thus producing secondary alcohols (except in the case of methanol), or from the adjacent carbon, producing primary alcohols.

(3) Hydrogen separates most readily from a CH_2 group, with more difficulty from a CH_3 group, and not at all from a CH group. Mixtures of higher alcohols are obtained by treating ethyl alcohol with dehydrating metals and alkaline earth oxides at high temperature and pressure. For instance, ethyl alcohol, heated in an autoclave to 300°C with copper and CaO, yields butyl alcohol, hexyl alcohol and octyl alcohol. The amount of metal should not exceed 5 per cent.

Butyl alcohol, containing small quantities of other oxygenated products, is produced by passing vapors of ethyl alcohol at 10 to 100 atmospheres pressure at a velocity of at least 20 mols per hour, per litre of catalyst, over a catalyst containing at least 60 per cent of magnesium compounds, or mixtures of magnesium compounds with compounds of other light metals, together with a small proportion of Cu, Ag, Mn, Fe, Cr, W, Zn, Sn, Ni, or Co, or a compound of these metals.[24]

Butyl alcohol and isobutyl alcohol are produced by vapor phase reaction from a mixture of methyl alcohol, ethyl alcohol and hydrogen over a heated (200 to 400°C) contact material consisting of a large proportion of magnesium oxide, together with one or more of the oxides of Pb, Th, Ag, U, Cd, Sn, Mn, Zn, Fe, Ni, or Cu.[24] These methods are of interest in making higher-boiling solvents from the less expensive methyl and ethyl alcohols.

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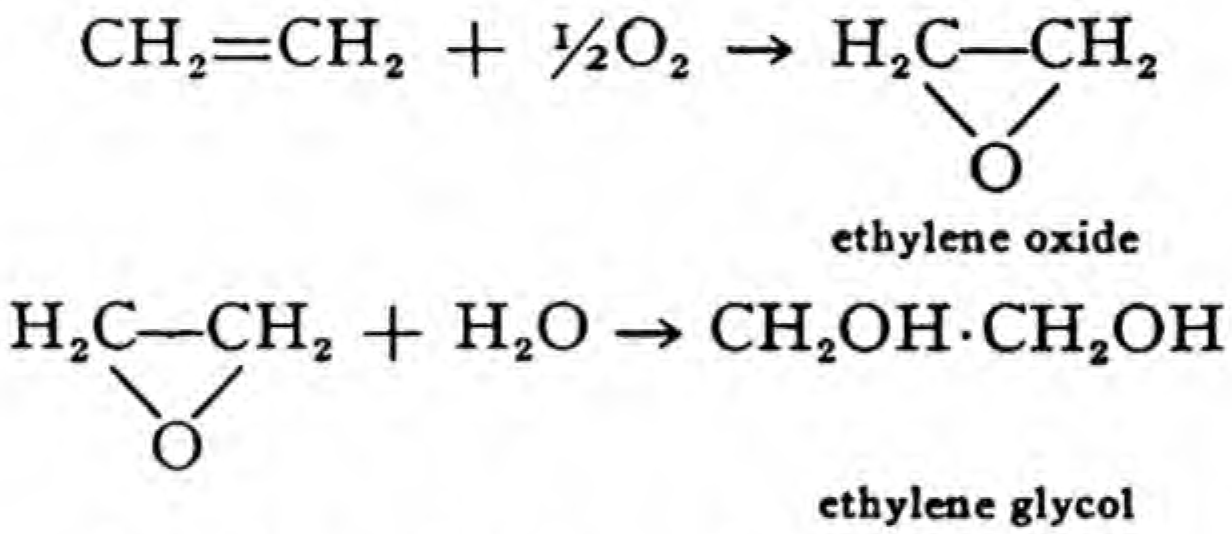
[24] German Patent 478,141 (1938) (Deutsche Gold-und Silberscheideanstalt vorm. Roessler).

Ethylene glycol is formed from ethylene, oxygen, and water in the presence of catalysts presumably according to the following simple scheme: [26]



$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \rightarrow H_2C{-}CH_2\ (\text{O bridge})$$

$$H_2C{-}CH_2\ (\text{O bridge}) + H_2O \rightarrow CH_2OH{\cdot}CH_2OH$$

As catalysts for the oxidation of ethylene to ethylene oxide, which, in turn, is hydrated to ethylene glycol, silver, obtained by reduction of silver compounds by hydrogen or by reducing agents (hydrazine, formaldehyde, glucose, hydroxylamine, phenylhydrazine), serves well. With this catalyst, olefin oxides are obtained at 150–500°C temperature and 5–20 atm. pressure. Ethylene oxide is formed by oxidation of ethylene between 300–400°C in the presence of a catalyst made from the formate, acetate, or oxalate of silver on active charcoal or silica gel.[27] A mixture of ethylene and oxygen is passed over alumina and silver to form ethylene oxide, which is selectively adsorbed from the mixture and the latter recycled.[28] In one process, ethylene oxide is cooled to below its boiling point and is passed continuously into an unheated reaction vessel, together with sufficient water to form 10–15 per cent by volume of an aqueous solution of glycol, on the hydration of all of the olefin oxide in the presence of 0.1–0.5 g of sulfuric acid per 100 cc of the aqueous gycol solution. The gycol solution is continuously withdrawn.[29] Ethylene oxide is brought to react with water at 50–100°C under pressure, in the presence of iron formed in situ by the action of one of the components in the reaction system on bodies of iron, e.g., Raschig rings.[30]

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[26] German Patents 561,049 (1930) and 619,195 (1935); U. S. Patents 1,982,545 (1934) and 1,998,878 (1935) (Reissue 20,370, 1937).

[27] N. V. de Bataafsche Petroleum Maatschappij.: British Patent 434,011 (1935).

[28] Carter: Canadian Patent 387,564 (1940).

[29] Eoff, Linder, and Beyer: *Ind. Eng. Chem.,* 11, 842 (1919).

Glycerol and propylene glycol are formed by hydrogenation of glucose and other sugars in the presence of mixed catalysts of copper and nickel or copper and cobalt, the catalyst being fed into the reaction chamber in an unreduced state. The hydrogenation is carried out at temperatures below 240°C in successive short stages, the duration of any one stage being no more than one-half of the starting material is reduced. The hydrogenated products are fractionated at diminished pressure to separate the glycerol and the glycol, and the residue is returned for further hydrogenation.[31] Propylene and ethylene glycols and glycerol are claimed to be formed by bringing a monosaccharide into contact with a tertiary amine, such as pyridine, at a temperature of about 75–150°C, and then subjecting the resulting mixture to hydrogenation in the presence of Raney's nickel catalyst.[32] Glycerol may also be produced by fermentation of sugar.[29]

The processes, discussed in this section, are only examples taken from a multitude of published references. Especially for production of higher alcohols, glycols, and glycerol,[34] the developments in the last ten years have been very considerable.

GENERAL REFERENCES

Patart: *Compt. rend.*, **179**, 1330 (1924); *Chimie et industrie*, **13**, 179 (1925); Lush: *J. Soc. Chem. Ind.*, **46**, 454T (1927); Clough and Johns: *Ind. Eng. Chem.*, **15**, 1030 (1923); Elkington: British Patent 341,167 (1930); German Patent 637,909 (1936) (A.-G. für Zellstoff und Papierfabrikation); Fuchs and Querfurth: U. S. Patent 2,050,788 (1937); Joshua, Stanley, Fuchs, Querfurth and Dymock, U. S. Patent 2,094,297 (1937); Cohen and Beamer: U. S. Patent 2,255,411 (1941).

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[30] Reynhart: U. S. Patent 2,236,919 (1941).

[31] Parodi-Delfino: Swiss Patent 213,251 (1941); *Chem. Abstracts*, **36**, 3386 (1942).

[32] Hanford: U. S. Patent 2,209,055 (1941).

[34] E. C. Williams, *Trans. Am. Inst. Chem. Eng.*, **37**, 157 (1941); *Chem. & Met. Eng.*, **48**, 87 (1941) (Production of glycerol); Metzger, U. S. Patents 2,050,442 and 2,050,443 (1936) (alcohol from ethylene).

6. Cracking of coals, tars and oils by hydrogenation at high temperatures and pressures

When hydrocarbons are subjected to high temperatures, the molecules decompose forming radicals ($-CH_3$, $=CH_2$, $\equiv CH$), which combine to form new molecules, a matter which has been discussed in detail by Rice et al.[1]

The decomposition of petroleum vapors, above dull red heat, to form a hydrocarbon mixture of a composition differing from that of the original mixture was discovered accidentally in Newark, N. J., in 1861.[2]

The decomposition of organic compounds, under pressure, was observed by Ipatieff,[3, 4] about 1904. This work was later followed up with studies on organic decompositions under pressure which, in part, was due to hydrogen introduced from the outside.

Bergius [5, 6] discovered in 1913 that it was possible to add hydrogen to coals by treating them between 300 and 500°C at 100 to 200 atmospheres of hydrogen pressure. Later (1921) it was shown that 200 atmospheres pressure of hydrogen at 400°C and about two hours' time of contact constituted the most favorable conditions for the majority of coals investigated at that time. Still later, the I.G. Farbenindustrie A.-G.,[7] in Germany, developed the hydrogenation-cracking process of coal to a commercial scale, using contact catalysts to facilitate the conversion. Actually, already Bergius had used natural iron oxide (Luxmasse) to desulfurize the oils, before cracking and this oxide also acts as a catalyst. The Imperial Chemical Industries, Ltd.,[8] England, started research on hydrogenation-cracking of coal in 1927, and at about the same time the Standard Oil Company of New Jersey acquired the I.-G. Farbenindustrie process for cracking of petroleum. Since then, hydrogenation-cracking has been widely studied by the oil companies and by the United States and Canadian governments.

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[1] Rice et al.: *J. Am. Chem. Soc.*, **54**, 3529 (1932); *ibid.*, **55**, 3035 (1933); *ibid.*, **56**, 284, 2105, 2472, 2497 (1934).

[2] Sabatier, P., and E. E. Reid: *Catalysis in Organic Chemistry*, New York, D. Van Nostrand Co., 1923.

[3] Ipatieff: *Ber.*, **37**, 2961, 2986 (1904).

[4] Ipatieff, V. N.: *Catalytic Reactions at High Pressures and Temperatures*, New York, The Macmillan Company, 1937, p. 373.

[5] Bergius: British Patents 4574 (1915) and 18,232 (1915).

[6] Bergius: *Proc. World Petroleum Congress*, Vol. "F", p. 282, 1933.

[7] I. G. Farbenindustrie A.-G.: British Patent 247,583 (1927).

[8] Gordon: *J. Inst. Fuel*, **9**, 69 (1935); Hilditch and Hall: *Catalytic Processes in Applied Chemistry*, London, Chapman and Hall Ltd. (1937).

Extensive study of destructive hydrogenation of organic compounds, as Ipatieff[4] terms the hydrogenation-cracking process, has been made by various workers, notably by Ipatieff et al.,[4, 10] Orloff et al.,[11] Kling and Florentin,[12] Hall,[13, 14] and others.

In the destructive hydrogenation of aromatic hydrocarbons above 400°C, under high initial pressure (65–100 atm.), in the presence of various catalysts, Ipatieff concludes that the combination of hydrogen with aromatic compounds occurs first, to be followed by the decomposition of the hydrogenated product. Also, active catalysts may hydrogenate a benzene ring at the time of its formation and during the decomposition of the hydrogenated product of a polynuclear aromatic hydrocarbon.

Kling and Florentin[12] draw the conclusion that at a definite temperature, specific for every complex molecule, it begins to disintegrate, and that this specific decomposition temperature, in most cases, is coincident with the temperature at which the fragments of the original molecule combine with hydrogen. In view of the fact that free radicals of short life are formed under pyrolytic conditions, this conclusion appears to be reasonable.

According to Hall,[13] the side chains of aromatic hydrocarbons become shortened and finally removed by destructive hydrogenation at temperatures above 450°C:

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[9] Hilditch, T. P., and C. C. Hall: *Calalytic Processes in Applied Chemistry*, London, Chapman and Hall Ltd., 1937.

[10] Ipatieff and Orloff: *Ber.*, **60**, 1963 (1927).

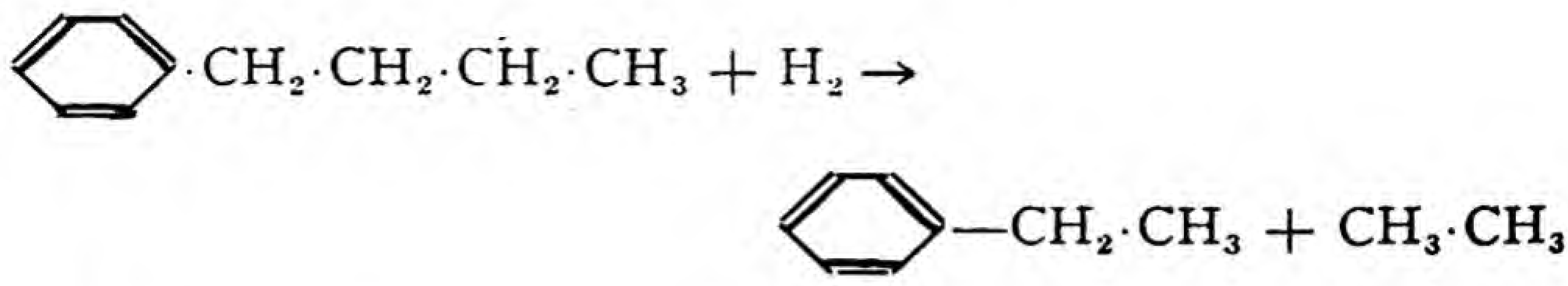
[11] Orloff et al.: *Ibid.*, **62**, 719, 1226 (1929).

[12] Kling and Florentin: *Compt. rend.*, **182**, 526 (1926).

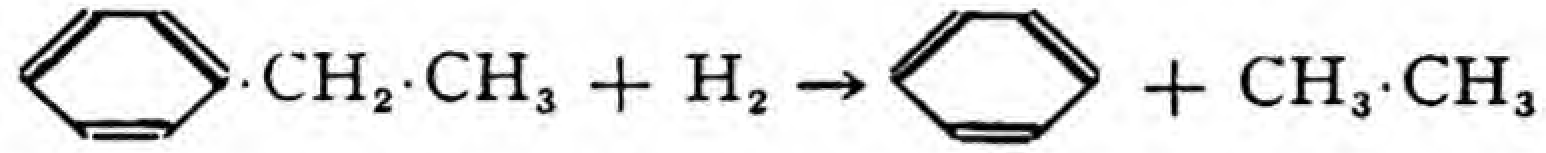
[13] Hall: *J. Soc. Chem. Ind.*, **54**, 208T (1935).

[14] Hall: *Fuel*, **12**, 76 (1933).

1.

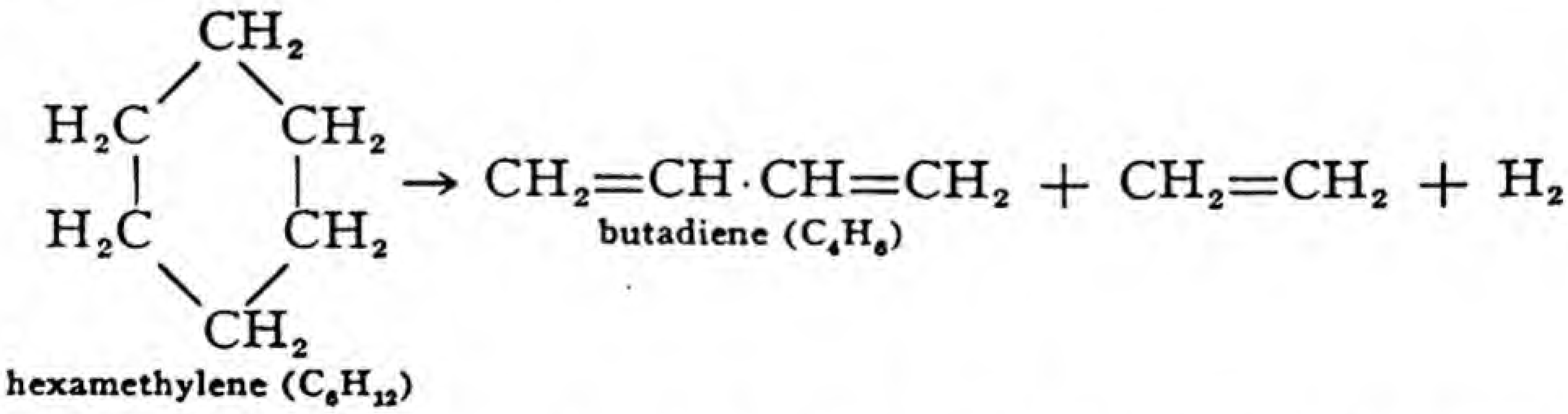

·CH₂·CH₂·CH₂·CH₃ + H₂ →
—CH₂·CH₃ + CH₃·CH₃

2.


·CH₂·CH₃ + H₂ →
+ CH₃·CH₃

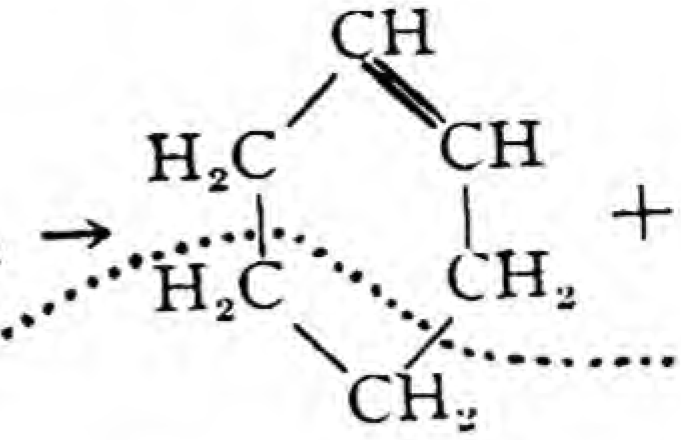
Schmidt[14a] states that metal oxides, which readily give off electrons, facilitate the breaking of bonds in the cracking process. This process is not primarily a process of rupture of C—C bonds as, in most cases, more C—H bonds are ruptured under the formation of double bonds (C=C). The C=C bond increases the strength of the C—C bonds next to it, but weakens the second next C—C bond, e.g.: $\mathrm{C\underset{1}{=}C\underset{2}{-}C\underset{3}{-}C-}$ and $\mathrm{-C\underset{3'}{-}C\underset{2'}{-}C\underset{1}{=}C\underset{2}{-}C\underset{3}{-}C-}$

The strength of the bondings 2 and 2′ is increased, and the strength of the bondings 3 and 3′ is decreased. The result is that by cracking of straight-chain paraffins, an almost equimolecular mixture of paraffins and olefins is obtained in the primary reaction, and the secondary reaction yields various amounts of hydrogen:


CH₂
H₂C
CH₂
H₂C
CH₂
CH₂
hexamethylene (C₆H₁₂)
→ CH₂=CH·CH=CH₂ + CH₂=CH₂ + H₂
butadiene (C₄H₆)

Actually, this process takes place with intermediate formation of tetrahydrobenzene (C_6H_{10}):

[14a] Schmidt: *Z. Elektrochem.*, 39, 824, 969 (1933).

1. $C_6H_{12} \rightarrow$  $+ H_2$

2. $C_6H_{10} \rightarrow C_4H_6 + C_2H_4$

Propylene is formed by side reactions.[14a]

Of more recent date are the researches by Adkins[15] which have been mentioned elsewhere, (see page 219), and which have considerable industrial possibilities.

The kinetics of hydrogen consumption, oxygen removal (principally as water), and liquefaction of a Pittsburg seam coal has been studied by Storch.[16, 17] 100 grams of coal ground to 200 mesh were mixed with 100 grams tetrahydronaphthalene and 1 gram stannous sulfide, hydrogen being added until the pressure at 20°C was 1000 lb per square inch. The time, temperature, and yields were as follows:

Temperature °C	Time hours	Conversion per cent of dry, ash-free coal: Based on residue found	Conversion per cent of dry, ash-free coal: Based on residue calculated from ash content
445	3	85.8	82.9
430	3	92.8	90.3
430	6	92.5	91.9
415	15	93.3	93.4
400	1	74.6	69.6
400	15	...	93.3
385	15	91.0	92.2
370	3	...	45.5
370	6	73.8	71.5
370	9	90.1	89.6
370	12	90.2	89.6

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[15] Adkins, H.: *Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts,* Madison, The University of Wisconsin Press, 1937.

[16] Storch, H. H.: *Contact Catalysis in the Hydrogenation of Coal, Coal Tar, and Oil,* Twelfth Report of the Committee on Catalysis, National Research Council, New York, John Wiley & Sons, Inc., 1940, p. 82.

[17] Storch: *Ind. Eng. Chem.,* **29,** 1367 (1937).

Temperature °C	Time hours	Conversion per cent of dry, ash-free coal Based on residue found	Based on residue calculated from ash content
370	15	90.7	89.6
355	3	...	33.1
355	9	...	81.6
340	9	50.9	48.3
310	3	26.3	14.7
310	9	23.8	19.8

This important investigation is summarized as follows:

1) The hydrogen consumption versus time curves are straight lines whose slope shows a temperature coefficient of 1.2 per 10°C. It is suggested that the diffusion of hydrogen, through a liquid film surrounding the catalyst surfaces, is the factor controlling the rate of hydrogen consumption. This is supported not only by the low-temperature coefficient and the approximately constant rate of consumption with varying time, but also by the lack of dependence of the hydrogen-consumption rate on other essential factors, such as rate of oxygen removal and rate of liquefaction.

2) A study of the oxygen-elimination rates, at various temperatures, shows that the main reaction is a thermal decomposition of the coal substance that results in the rapid elimination of about 60 per cent of the oxygen. This reaction has a relatively high activation energy. A second reaction, with a considerably lower reaction energy, is responsible for the slower elimination of the remaining 40 per cent of the oxygen. This reaction is probably a contact catalytic process. A third reaction is the condensation of the liquefied coal substance to form more stable molecules. This process becomes appreciable at temperatures above 400°C, and results in apparent negative temperature coefficients for the second oxygen-eliminating reaction.

3) From a similar study of the rates of liquefaction of the coal at various temperatures, at least four processes appear to be involved:

a) Solution or extraction of the coal substance. This is practically the only process occurring below 370°C. Its temperature coefficient is about 1.2 per 10°C, and it is probably a diffusion of dissolved material away from the surface of the coal.

b) A thermal decomposition of the coal substance above 370°C, involving the elimination of about 60 per cent of the oxygen of the coal.

c) The production of hydrocarbon gases (mainly methane and ethane), probably by catalytic hydrogenation of dissolved coal in the range of 370–415°C and mainly by thermal decomposition of dissolved coal above about 415°C.

d) The condensation of dissolved coal substance to form molecules more stable than the original coal. These molecules subsequently lose hydrogen, largely by methane formation. Above 440°C, this process results in coke formation, even under 180 atmospheres of hydrogen pressure.

On the basis of this reaction mechanism, Storch[16] concluded that the chief function of catalytic destructive hydrogenation is to saturate the free radicals or unsaturated compounds formed by the thermal decomposition of the coal, and also to hydrogenate the carbon-to-oxygen and double bonds in the later stages of the liquefaction. Storch also states that these reaction mechanisms require further elucidation.

Liquid-phase destructive hydrogenation. In the original Bergius process, the coal is powdered and mixed with a heavy oil which is obtainable from the process itself. 100 parts of finely powdered coal were made into a paste with 40 parts of heavy oil or tar and five per cent of Luxmasse, this mixture being pumped through the converters, together with hydrogen at 150–200 atmospheres pressure and a temperature of 450°C; 1000 lb of bituminous coal, after absorbing 50 lb of hydrogen, yielded by this process:[5, 6, 9]

150 lb	neutral, refined gasoline of 30–200°C boiling point
200 lb	"Diesel" oil
140 lb	fuel oil
240 lb	coke and ash
5 lb	ammonia

According to Storch,[16] powdered coal is hydrogenated by mixing it with a heavy oil and about 0.1 per cent of a catalyst (tin oxalate or sulfide), which, along with hydrogen at 200 atmospheres pressure, is passed through a preheater where it is heated to 450°C and then passed through three converters in series, the total contact time being about two hours. This hydrogenation mixture would lend itself excellently to phase studies. The catalytic action of the converter walls is quite substantial when of metal, whereas a wall, lined with Pyrex glass, shows no wall catalysis.

Vapor phase destructive hydrogenation. Low-temperature coal tars are hydrogenated, at low temperature, in the vapor phase. This reaction is catalyzed by small amounts of halogens, halogen compounds, and sulfides of molybdenum, tungsten and tin.[16, 17, 19, 20] Interestingly, hydrogen sulfide, in substantial partial pressure, appears to be beneficial for this conversion, probably by preventing the catalyst sulfides from being converted to oxides.[18] Nyrop [20] states that sulfur, in these reactions, acts as a carrier of hydrogen.

Hydrogenation experiments on American coals.[21] In studying the behavior of the banded constituents of coal, during liquefaction of fusain (100 grams) by hydrogenation at 400,[22] 415 or 430°C with an initial (cold) hydrogen pressure of 1000 lb per square inch, in the presence of tetrahydronaphthalene (100 grams) and stannous sulfide (1 gram), appreciable liquefaction was effected of seven fusains, two samples being liquefied to the extent of about 25 per cent. The hydrogenation proceeds readily to a certain point and then becomes difficult, indicating that fusain comprises two major components. The fusains contained from 88.1 to 93.5 per cent carbon and 2.8 to 3.5 per cent hydrogen (dry, ash-free basis).

In liquid-phase hydrogenation of Pittsburg seam coal,[21] it was found that the optimum conditions for Bruceton coal are about 440°C, 200–300 atmospheres pressure, and 2.75 hours contact time. The yield was 66 per cent of "middle" oil (containing 20 per cent boiling in the gasoline range and 80 per cent boiling below 330°C), and 20 to 25 per cent of hydrocarbon gases (methane to butane), obtained in a single pass through the converter. The loss consisted of 6–8 per cent of unreacted carbonaceous material and 3–6 per cent of oxygen, nitrogen, and sulfur hydrogenated to water, ammonia, and hydrogen sulfide. The charge used consisted of pulverized coal (98 per cent passing a 200 mesh screen). 42–47 per cent by weight of this coal is pasted with oil, the catalyst being 0.5 per cent each of stannous sulfide and molybdic acid (calculated on the weight of coal).

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[18] *British Fuel Research Board reports,* 1935–36; 1936–37; H. M. S. Office, London, 1936 and 1937, respectively.

[19] Varga and Makray: *Brennstoff-Chem.,* **17,** 81 (1936).

[20] Nyrop, J. E.: *The Catalytic Action of Surfaces,* London, Williams & Norgate Ltd., 1937.

[21] Storch et al.: *Ind. Eng. Chem.,* **31,** 190 (1939); *ibid.,* **31,** 869 (1939); *ibid.,* **31,** 1155 (1939); *ibid.,* **32,** 73 (1940); *ibid.,* **32,** 864 (1940); *ibid.,* **32,** 1372 (1940); *ibid.,* **33,** 1068 (1941).

[22] Graham and Skinner: *J. Soc. Chem. Ind.,* **48,** 129T (1929).

In studying the hydrogenation of attrital matter and anthroxylon, to 100 grams coal (200-mesh), 100 grams tetrahydronaphthalene, and 1 gram stannous sulfide were added hydrogen until a pressure of 1000 pounds per square inch, at 20°C, was reached. This mix was heated to 430°C during about one and a half hours, and kept at this temperature for three hours, with the exception of some samples, which were hydrogenated with better result at 400°C, and some at higher pressure (1800 pounds) and longer duration contact (six or nine hours). The hydrogenation data were:

Sample	Petrographic constituent	Residue yield, % (dry, ash-free basis)
A_1	Anthraxylon	1.1
C_1	Anthraxylon	4.2
C_2	Attritus {48% translucent; 50% opaque; 2% fusain}	24.3

In calculating these data, it is assumed that fusain is completely resistant to, (see above) and all constituents, other than opaque attritus, are completely liquefied by hydrogenation.

Samples of splint coal [21] were hydrogenated (100 g coal—200 mesh; 100 g tetrahydronaphthalene; 1 g stannous sulfide, pressure at 20°C: 1000 lb per sq in.; 1½ hours of heating to 430°C, maintained 3 hours). The conversion of the pure coal, on a dry ash-free basis, was for eleven samples from 57.5 to 86.7 per cent. This rather low conversion confirms the prevailing opinion that splint coals are not so suitable for hydrogenation as bright coals.

High-volatile bituminous coals [21] were hydrogenated (50%

through 200 mesh sieve, the balance < 80 mesh; catalyst, 0.5% stannous sulfide and 0.5% molybdenum trioxide). The yield data, estimated for industrial operation were, as follows:

Sample
1. High-volatile A washed bituminous coal from Alabama
2. High-volatile B bituminous coal from Illinois
3. High-volatile non-coking bituminous coal from Washington

	Reaction pressure lb/sq in.	Reaction temperature, °C	Hydrogen absorbed % of moisture- and ash-free coal	Tons oil/100 tons of moisture- and ash-free coal	Dry coal	Coal as mined
1.	4000	430	8.6	59.8	54.2	51.4
2.	3200	430	8.0	70.5	65.4	60.4
3.	3200	430	7.5	68.5	65.8	59.4

Samples of sub-bituminous coals, from Colorado, Wyoming and Montana and of lignites from North Dakota, were hydrogenated with the following results: [21]

1. Sub-bituminous coals
    (a) Puritan Mine, Colorado
    (b) Monarch No. 45, Wyoming
    (c) Rosebud, Colstrip, Montana
2. North Dakota Lignite
    (a) Beulah Lignite
    (b) Velva Lignite

	Run No.	Reaction pressure lb/sq in.	Temperature, °C	Hydrogen absorbed % of moisture- and ash-free coal	Tons oil/100 tons of moisture- and ash-free coal	Dry coal	Coal as mined
1a	27–11	3300	436	8.6	64.1	60.4	46.0
1b	46–2	3300	430	6.8	66.0	62.6	48.1
	47–5	4600	434	8.6	66.5	63.1	48.5
	48–2	4600	430	7.9	67.5	64.0	49.2
1c	50–7	4600	433	7.9	63.2	57.0	42.7
2a	31–7	3300	430	8.0	53	46	30
2b	55–9	4500	433	7.1	54	50	30

In runs 48-2 and 50-7, 0.05 per cent iodoform plus 0.1 per cent SnS were used as catalyst instead of 0.5 per cent each of MoO_3 and SnS used in runs 27-11, 46-2 and 47-5. As catalyst for the Beulah lignite (31-7) were used 0.5 per cent MoO_3 plus 0.5 per cent SnS, and for the Velva lignite 0.05 per cent iodoform with 0.1 per cent SnS. Considering the vast resources of sub-bituminous coal and lignite in the Middle West of this continent, these investigations, which are excellently detailed, are highly significant.

All these investigations are summarized in a later publication, i.e., the data from hydrogenation of light bituminous coals, three sub-bituminous coals and two lignites. It is noteworthy that the yield of tar acids increases with decreasing rank of the coal from about 6 per cent (of the moisture- and ash-free coal) for the high-volatile bituminous coals of highest rank to about 16 per cent for sub-bituminous coals of lowest rank and for lignites. About half of the tar acids boil below 235°C at atmospheric pressure. Of these low-boiling tar acids, about 50 per cent is xylenols, 30 per cent cresols and 20 per cent phenol. The nuetral oil, boiling above 188°C, contains only small amounts of paraffins and consist mainly of aromatics and naphthenes. About 7 per cent of cyclic olefins is present. The neutral oil, boiling in the range 20–188°C, contains about 33 per cent saturated paraffins, 8 per cent olefins, 38 per cent naphthenes and 21 per cent aromatics. The yield of neutral oil is about 60 per cent (of the moisture-and ash-free coals) for bituminous coals, 50 per cent for sub-bituminous coals and 38 per cent for lignites.

Some interesting coal hydrogenation data were obtained by Berl, Biebesheimer, and Koerter,[23] who hydrogenated a bituminous coal and wood charcoal, the residue obtained by extracting bituminous coal with tetrahydronaphthalene under pressure at 250°C, and the bitumen extracted, the tetrahydronaphthalene being carefully removed from both fractions. Iron oxide, iron and iodine were used as catalysts. The data were as follows:

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[23] Berl, Biebesheimer, and Koerter: *Ind. Eng. Chem.*, 33, 672 (1941).

	Original bituminous coal	Residual coal	Bitumen
Hydrogen pressure, atm.	103	103	103
Temperature, °C	445/50	480	440/50
Time, minutes	120	120	120
Liquid hydrogenation products, per cent	49.6	53.46	96.6

As to charcoal from beechwood, practically no liquid reaction products are obtained, almost the entire yield being methane.

Hydrogenation tests with Canadian coals have been studied in a detailed way, theoretical as well as practical important data being obtained.[24, 25] The ground coal was mixed with an equal weight of oil, usually the fraction of the product from the preceding run boiling above 230°C. 5 per cent stannous oxide, calculated on the weight of the coal, was used as a catalyst. The pressure was 3,000 lb per square inch, the temperature 420°C. A summary of the data obtained is as follows:[24]

Assuming an average specific gravity of 1 for the primary oils, the yields of primary oil in terms of imperial gallons per short ton of dry and ash-free coal were as follows:

Sample No.	Rank of coal	Imperial gallons per 2,000 lb of dry and ash-free basis
1	British Columbia medium-volatile bituminous	124
2	British Columbia high-volatile bituminous A	134
3	England high-volatile bituminous A	143
4	Nova Scotia high-volatile bituminous A	154
5	British Columbia high-volatile bituminous B	148
6	Alberta high-volatile bituminous C	107
7	Alberta sub-volatile bituminous B	125
8	Alberta sub-volatile bituminous C	115
9	Saskatchewan lignite	113
10	Ontario lignite	111
11	Ontario peat	88

In these studies, detailed ash analyses were made, the conclusion being drawn that there was no evidence of catalytic activity in any constituent of the ashes. Consequently, trials with hydrochloric acid as a catalytic agent did not indicate any improvement above standard operating conditions.

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[24] Warren, T. E., and K. W. Bowles: *Tests on the Liquefaction of Canadian Coals by Hydrogenation,* Canada Department of Mines and Resources, Mines and Geology Branch, Bureau of Mines, Publication No. 798, 1938.

[25] Warren, Bowles, and Gilmore: *Ind. Eng. Chem.,* **31**, 1021 (1939).

Hydrogenation of a high-temperature tar, distilled to 230°C to remove water and valuable tar acids and solvents, has been carried out by Storch et al.[26] It was shown that two stages of hydrogenation are required: (1) Liquid-phase hydrogenation in which the tar is mixed with a small amount of catalyst and pumped into the converter along with hydrogen under pressure. (2) Vapor-phase hydrogenation in which the 210–300°C fraction of the liquid-phase product is vaporized in a stream of hydrogen and passed through a bed of catalyst particles about ⅛ inch in diameter.

The temperature and contact times, in the liquid phase, are about 450°C and two hours, and in the vapor phase, 510°C and half a minute, respectively.

The converters, used in the liquid-phase trials, were identical with those used for coal hydrogenation studies by Storch et al. Two converters were connected in series, the temperature in the first being 400°C and in the second 450–460°C, and the pressure 4500 lb per square inch in both; 0.5 per cent ammonium chloride with 0.5 per cent of stannous sulfide was used as catalyst.

In the vapor-phase operation, alumina gel, impregnated with equal weight of ammonium molybdate, was used as catalyst.

Products from hydrogenation of topped high-temperature tar were as follows: (in volume per cent)

	Yield based on topped tar		
	From liquid-phase hydrogenation	From vapor-phase hydrogenation	Total recycle yield
Phenol	0.27	0.0	0.27
Cresol	0.76	0.0	0.76
Benzene	0.51	1.19	1.70
Toluene	1.69	3.98	5.67
Xylene	1.87	4.00	5.87
Tetrahydronaphthalene	1.40	9.60	11.00
Cyclohexane	0.59	1.56	2.17
Methylcyclohexane	1.18	2.35	3.51
Dimethylcyclohexane	0.59	0.91	1.50
Total chemicals listed	8.86	23.59	32.45
High-flash naphtha	18.64	47.41	66.05
Total oil distilling to 207° C	27.50	71.00	98.50

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[26] Storch, Hirst, Fisher, Work, and Wagner: *Ind. Eng. Chem.*, **33**, 264 (1941).

Tar hydrogenation undoubtedly has a considerable future in the United States.

Finally, the hydrogenation of wood tar has been investigated by Morrell and Egloff,[27] who hydrogenated Douglas fir wood tar at temperatures from 393 to 405°C and pressures of 75, 100, and 120 lb per square inch. The yield of motor fuel, free from tar acids, was approximately 26 per cent (based on the dry wood tar). The anti-knock properties of the hydrogenated product were better than those of benzene. The motor fuel thus obtained had a content of 97.2 per cent aromatic and unsaturated hydrocarbons, and only 2.8 per cent of paraffins and naphthenes. The content of tar acids in the tar was about 5 per cent. A hardwood tar, hydrogenated at 382°C and 90 lb pressure per square inch, yielded about 24 per cent motor fuel.

It seems to be appropriate to finish this section with a table by Pier [28] presenting data for the properties of gasoline (motor spirits) from different raw materials:

Middle oil from	Sp. gr.	Octane number
Paraffin	0.680	45
Mixed-base petroleum	0.722	64
Asphalt-base petroleum	0.728	67
Shale oil, paraffinic	0.712	65
Shale oil, asphaltic	0.732	66
Brown coal tar (low-temperature carbonization)	0.734	65
Liquefaction of brown coal	0.735	66
Petroleum crack residue	0.745	74
Liquefaction of coal and extract	0.745	74
High-temperature coal tar	0.748	75

GENERAL REFERENCES

H. H. Storch et al.: *Ind. Eng. Chem.*, **36**, 291 (1944) (Round Table Conference on "Hydrogenation of Coal"); King, J. G.: *The Hydrogenating-Cracking of Tars*, Science of Petroleum, Oxford University Press, 1938, p. 2156; *Fuel* **19**, 13, 51, 67, 132, 162 (1940); **20**, 5 (1941).

7. Production of motor fuels

The modern production of motor fuels is based upon ingenious use of catalytic processes, whereby it is made possible to utilize such resources as coal, lignite, natural gas, water gas, and refinery gases from petroleum as raw materials.

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[27] Morrell and Egloff: *Ind. Eng. Chem.*, **27**, 537 (1929).

[28] Pier: *Trans. Faraday Soc.*, **35**, 967 (1939).

Aviation Gasoline

a. *High-Pressure Hydrogenation Process* (Standard Oil Development Company)[1, 2, 3, 4]

The catalytic hydrogenation process developed by this company has been adapted to the manufacture of fuels for internal combustion engines as follows:[3]

"High-octane-number aviation gasoline production from kerosene and gas oil fractions.

Motor gasoline production from gas oils.

Aviation blending agent production by saturation of branched-chain polymers.

Production of high-grade Diesel fuels from low-quality gas oils.

Production of water-white paraffinic kerosenes from inferior-quality distillates.

Production of high-viscosity-index lubricating oils from poor-quality lubricating distillates.

Refining (or 'hydrofining') of gasolines to low sulfur content and high stability.

Conversion of asphaltic crudes and refinery residues into lower-boiling gas oils of increased paraffinicity.

Preparation of low-aniline-point, high-solvency naphthas.

Preparation of high-flash, high-octane-number safety fuels."

This company developed a high-pressure hydrogenation process, by which naphthas can be produced which are similar in stability and volatility to naphthas prepared by distillation of selected

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[1] Russell, R. P.: *The Hydrogenation of Petroleum*, reprinted from "The Science of Petroleum," Oxford University Press (Courtesy The Standard Oil Development Company).

[2] Murphree, Gohr and Brown: *Ind. Eng. Chem.*, 31, 1083 (1939).

[3] Murphree, Brown and Gohr: *Ibid.*, 32, 1203 (1940).

[4] Murphree and Barr: *Catalytic Hydrogenation Provides Low Cost Aviation Gasoline*, World Petroleum Annual Refinery Issue, 1940.

crudes, and which possess anti-knock properties superior, in general, to those of the natural naphthas. Synthetic polymers also can be hydrogenated, under high pressure, to yield high-octane-number blending agents which can be incorporated in natural or hydrogenated napthas for the production of premium-grade aviation fuels of 100 octane number or above.[5]

In this process, the catalysts used possess the property of converting petroleum oils, boiling outside the naphtha range, into lower-boiling cyclic and branched-chain compounds which impart desirable high-octane values to the naphtha product. The catalysts are mechanically rugged, resistant to poisoning by sulfur, and can be kept in continuous operation for a year or more.[2]

Simple hydrogenation, i.e., the addition of hydrogen to a carbon to carbon double bond, and destructive hydrogenation, i.e., conversion of gas oils and heavy residues to light distillates, is used in this process.[3]

Simple hydrogenation, i.e., the addition of hydrogen to olefinic compounds, involves a free energy change for the hydrogenation of gaseous di-isobutylene to gaseous octane of $\Delta F^\circ = -28{,}570 + 27.6\ T$.[5] Accordingly, increasing temperature favors the less hydrogenated product, but at temperatures up to 150°C, the rate of reaction is low, except with extremely active and very sensitive catalysts. Commercial operation is conducted by using a nickel catalyst, which is regenerated, at temperatures from 180 to 190°C and pressures 1 to 4 atmospheres.[6] Nickel, however, is sensitive to sulfur, and sulfur-resistant catalysts may be used at higher temperatures and pressures, the latter being necessitated to suppress competing reactions. Such catalysts, as used by the Standard Oil Development Company, have been used in some cases for a year or longer (1940).

Destructive hydrogenation, i.e., the combined addition of hydrogen and cracking, is part of this processing:[7]

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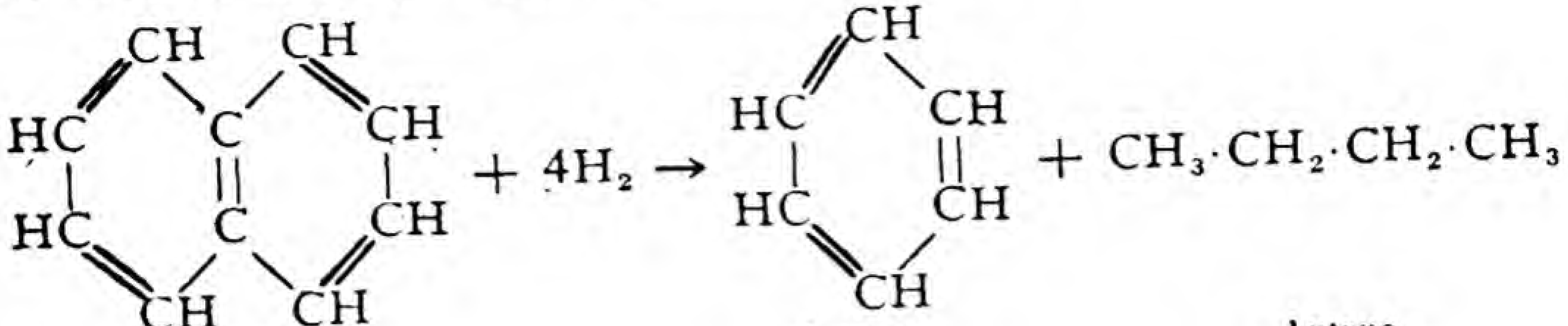
[5] Parks and Todd: *Ind. Eng. Chem.*, **28**, 418 (1936).

[6] Edlund: *Proc. Am. Petroleum Inst., 8th Mid-Year Meeting, III*, **87**, 1938.

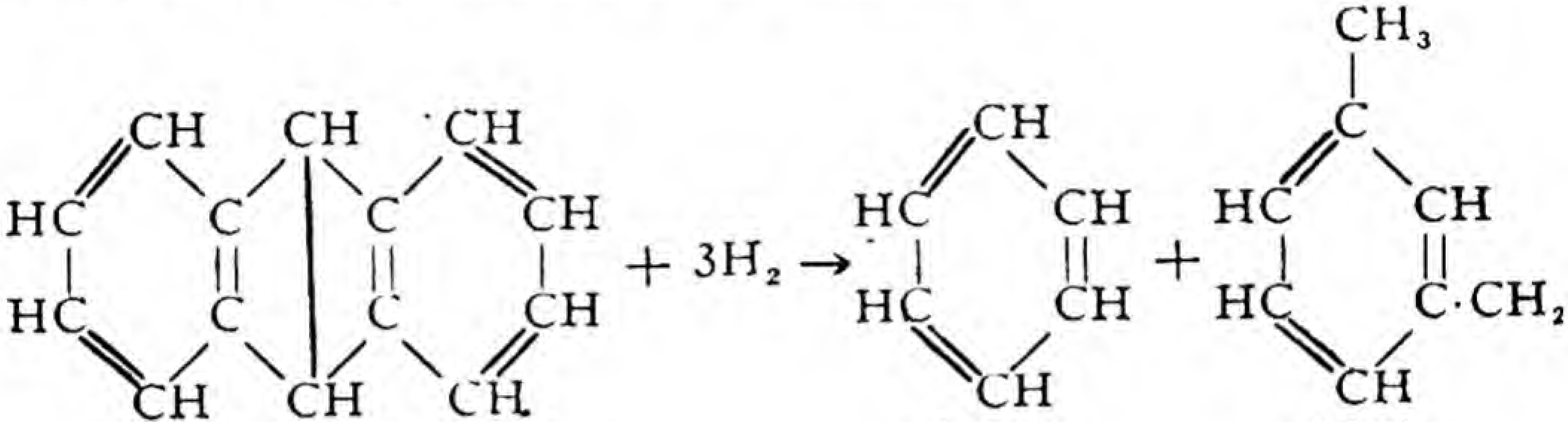
[7] Sweeney and Vorhies: *Ind. Eng. Chem.*, **26**, 195 (1934).

1. Destructive hydrogenation of naphthalene:



naphthalene benzene butane

2. Destructive hydrogenation of anthracene:



anthracene benzene toluol

The rupture of the polycyclic rings occurred at temperatures between 400 and 538°C. and a partial pressure of hydrogen of 10 to 50 atmospheres.

Napthalene, anthracene, or similar condensed aromatics are not formed from benzene and butane, benzene and m-xylene, or other similar compounds by hydrogenation, therefore, they are absent in destructively-hydrogenated petroleum fractions. High octane numbers in hydrogenated gasolines are attributed to branched-chain paraffins, naphthenes, and aromatics. Although some isomerization to such materials take place, feeds, which already contain such molecules, or compounds which are readily reduced to them on scission, are most suitable.

The hydrogen used is obtained by reacting natural gas or refinery gas with steam by a continuous two-stage process:

$$1.\quad CH_4 + H_2O \xrightarrow[\text{catalyst}]{\text{heat}} CO + 3H_2$$

$$2.\quad CO + H_2O \xrightarrow[\text{catalyst}]{\text{lower heat}} CO_2 + H_2$$

The CO_2 is removed by counter-current scrubbing in a bubble tower using ethanolamine as absorbent. The scrubbing liquor is treated with steam at atmospheric pressure to remove the O_2, and the ethanolamine solution is cooled, recycled to the bubble tower, and used over again. The CO_2 may also be removed by water scrubbing.

The manufacture of hydrogen and the aviation naphtha production by high-pressure hydrogenation are demonstrated in the following figures.

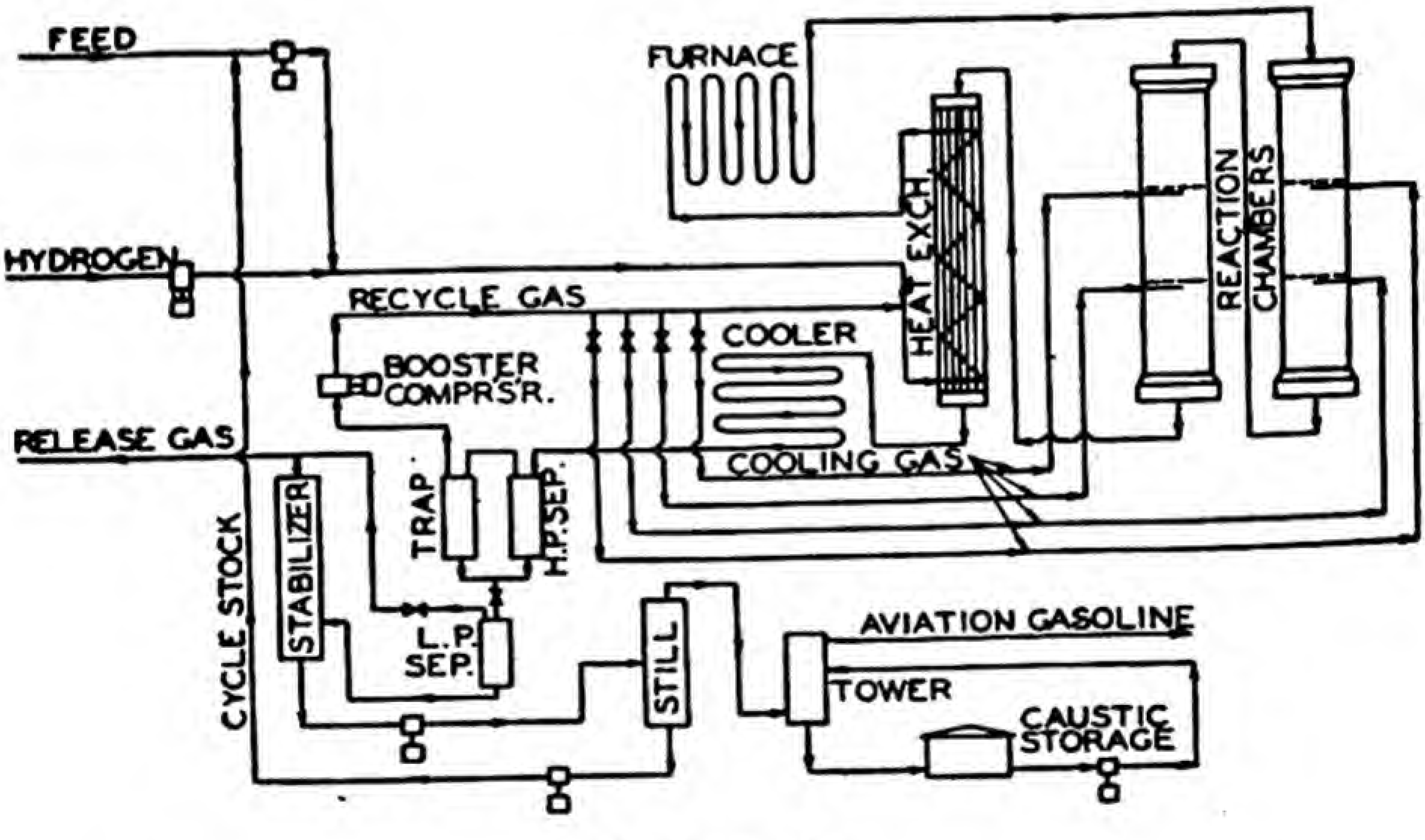

FEED
FURNACE
HYDROGEN
RECYCLE GAS
HEAT EXCH.
REACTION CHAMBERS
BOOSTER COMPRS'R.
COOLER
RELEASE GAS
COOLING GAS
TRAP
H.P. SEP.
CYCLE STOCK
STABILIZER
L.P. SEP.
STILL
AVIATION GASOLINE
TOWER
CAUSTIC STORAGE

FIGURE 21

FLOW DIAGRAM OF AVIATION NAPHTHA PRODUCTION BY HIGH-PRESSURE HYDROGENATION

(Murphree, Brown and Gohr)
(Reprinted by permission from *Ind. Eng. Chem.*, **31**, 1084 (1939); courtesy of Standard Oil Development Co., New York, N. Y.)

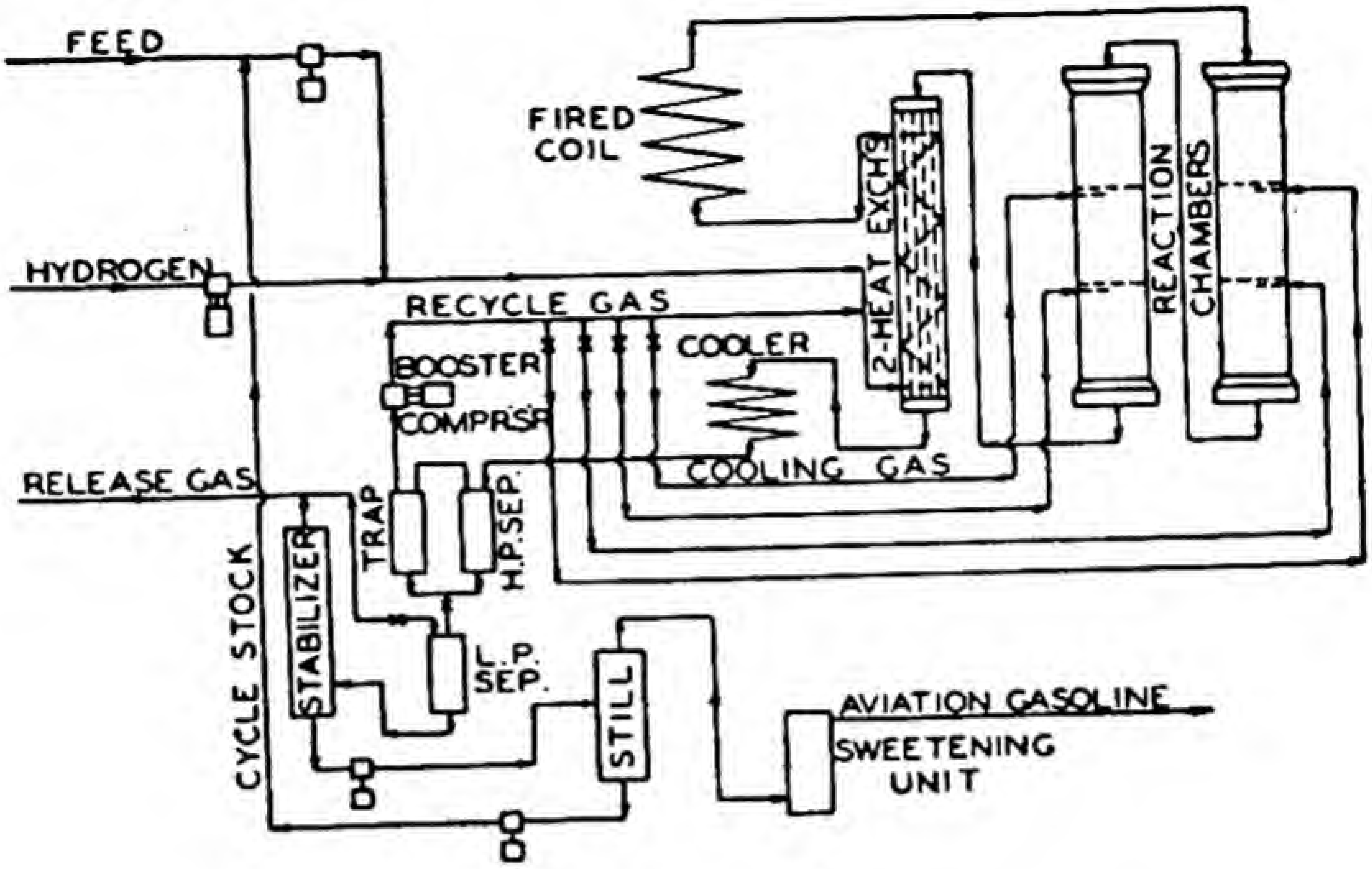

FEED
FIRED COIL
HYDROGEN
RECYCLE GAS
BOOSTER COMPRSR
COOLER
2-HEAT EXCH'S
REACTION CHAMBERS
COOLING GAS
RELEASE GAS
CYCLE STOCK
STABILIZER
TRAP
H.P.SEP.
L.P. SEP.
STILL
AVIATION GASOLINE
SWEETENING UNIT

FIGURE 22

FLOW SHEET OF HYDROGENATION SECTION

(Murphree, Brown and Gohr)
(Reprinted by permission from *Ind. Eng. Chem.*, 32, 1206 (1940); courtesy of Standard Oil Development Co., New York, N. Y.)

Cracking vs. Hydrogenation of West Texas Crude
(After Murphree, Brown and Gohr)

Type Operation	Thermal Cracking	Hydrogenation
Over-all yields on crude:		
Gasoline, vol. %	41.3	54.5
Heating Oil, vol. %	28.7	37.8
Heavy fuel oil, vol. %	26.4	9.4*
Gas, weight %	3.5*	1.8*
Runs per 10,000 barrels day of gasoline plus 6,940 barrels/day of heating oil:		
Crude consumed, barrels/day	24,000	18,350
Fuel oil produced, barrels/day	6,400	.....
Total feed to hydrogenation	.....	10,850
Inspections:		
Gasoline:		
Reid vapor pressure, lb/sq in.	10.0	10.0
Distillation, % over at:		
158° F (70° C)	20.7	21.2
212° F (100° C)	43.1	43.2
257° F (125° C)	67.9	66.6
A.S.T.M. Octane No.	69.6	66.0
C.F.R.—Research (1939) Octane No.	74.3	68.4

Type Operation	Thermal Cracking	Hydrogenation
cc $Pb(C_2H_5)_4$ to 81.5 C.F.R. Research (1939) Octane No.	1.5	1.5
Heating Oil, Gravity, ° A.P.I.	32.2	35.8
Fuel Oil:		
Gravity, ° A.P.I.	9.0	...
Viscosity, Saybolt Furol sec. at 122° F (50° C)	130	...

* Consumed to meet operating fuel requirements.

Tetraethyl Lead Susceptibility of Hydrogenated and Natural Aviation Fuels (After Murphree, Brown and Gohr[3])

	A.S.T.M. Octane No.	
cc $Pb(C_2H_5)_4$/gal	Hydrogenated aviation fuel	Natural aviation fuel
Clear	76.4	74.1
3	90.5	88.6
6	95.2	93.2
10	98.7	97.0

The Fluid Catalyst Cracking Process.[7a] When oils are cracked, the activity of the catalyst is reduced due to deposition of carbon on its surface, and the catalyst has to be regenerated by burning with air. In the fluid catalyst process, the regeneration of the catalyst has been made continuous, by using a finely powdered catalyst which is kept dispersed so that it can be handled substantially as a liquid. The catalyst is conveyed through the reactor by the oil vapor and is separated in dust recovery equipment, the product vapor flowing to a distillation apparatus.

The separated spent catalyst is collected in a hopper from which it flows, at high density, down a standpipe, and is injected into a stream of air that carries the catalyst to the regeneration vessel. From there, it flows into dust collecting equipment, where all of the catalyst is removed from the flue gas. The recovered catalyst is then collected in a hopper, flows down through a standpipe, and is injected into the oil stream, the cycle thus being completed. It follows that the process is completely continuous with respect to the flow of oil, air, and catalyst, and the operation of the fluid cracking plant is entirely automatic.

[7a] Murphree, Brown, Fischer, Gohr, and Sweeney: *Ind. Eng. Chem.*, **35**, 768 (1943).

Normal reactor temperatures lies in the range of 427 to 538°C; and the regeneration temperatures are maintained between 538 and 650°C. In most recent applications, for gas oil cracking, the pressure, at the top of the reaction vessel, is in the order of 10 lb per square inch, and the pressure at the top of the regeneration vessel is substantially atmospheric. This plant has been used for production of high quality motor gasoline, high-octane aviation gasoline, synthetic toluene, and raw materials for synthetic rubber. The gasoline (motor) has a clear octane number of 92–94 by the CFR research method.

b. *Low-Pressure Hydrogenation Process* (Shell Development Company and Shell Chemical Company)[8]

The search for a satisfactory gasoline of high anti-knock value, containing an optimum amount of lead and having a high calorific value, led to the development, by the Shell Companies, of a practical commercial process for the production of octanes of 98–100 octane number, by direct hydrogenation of an octene mixture, prepared by butylene polymerization, but the process is suited also to other feeds such as di-isobutylene and tri-isobutylene.

The hydrogenation process operates in the vapor phase at 1 to 4 atmospheres pressure, and at a temperature normally below 200°C. A suitable active nickel catalyst is used, which will hydrogenate octene vapors as they are passed over it, with the consumption of only a small stoichiometric excess of hydrogen.

During the years 1935–1938, the Shell Companies, in the United States, produced by this process more than 10,000,000 gallons of octanes (of 90–100 octane number).

Process theory. Thermodynamically, the conversion of octenes to octanes may be accomplished completely and readily by passing a mixture of octene and hydrogen over a suitable catalyst at atmospheric pressure and room temperature.

---

[8] *The Catalytic Hydrogenation of Octenes to Octanes,* a contribution by the combined staffs of the Shell Development Company and Shell Chemical Company, reprint, paper for presentation at 8th Mid-Year Meeting of Am. Petroleum Inst., May 24, 1938.

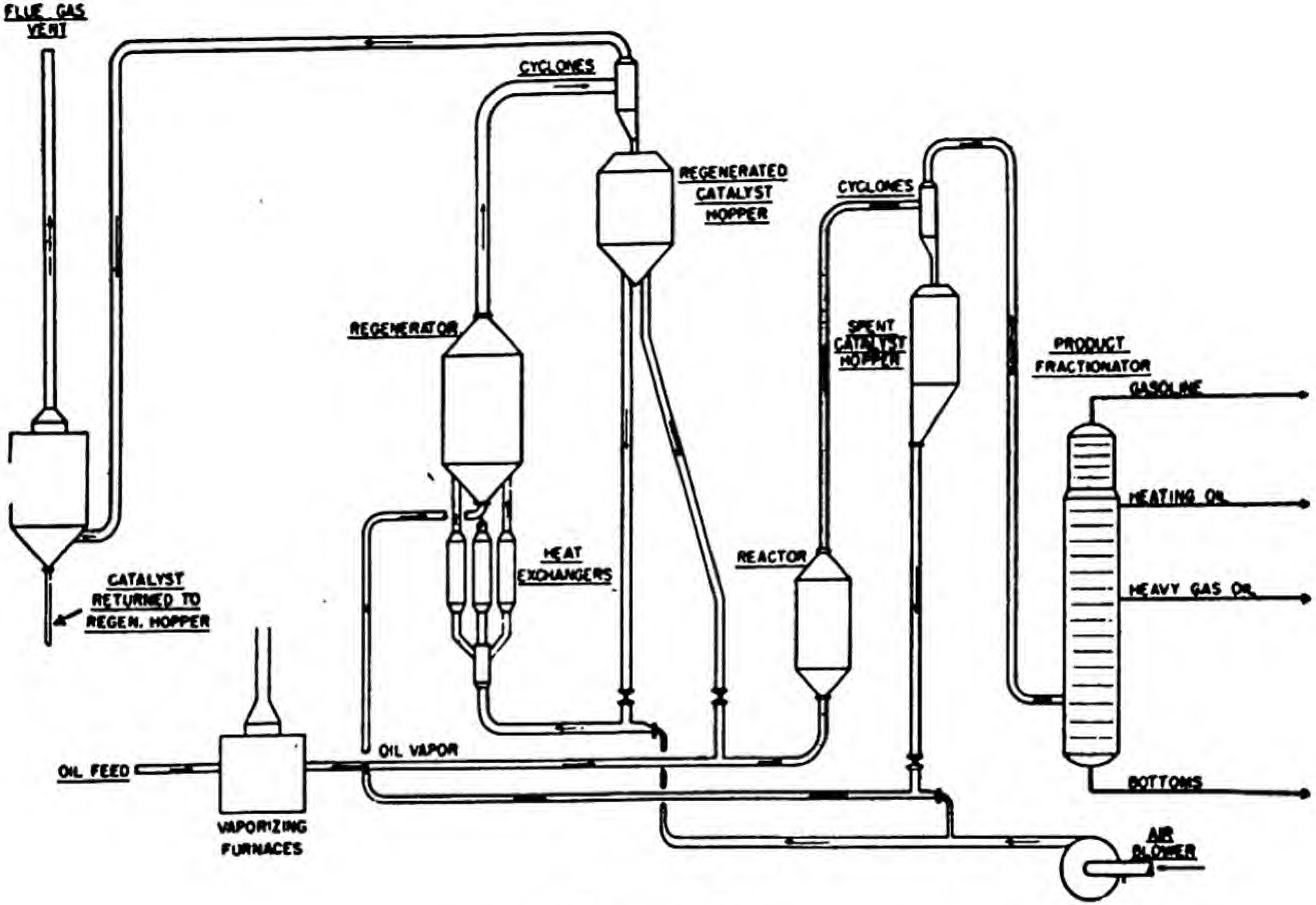

FLUE GAS VENT
CYCLONES
REGENERATED CATALYST HOPPER
CYCLONES
REGENERATOR
SPENT CATALYST HOPPER
PRODUCT FRACTIONATOR
GASOLINE
HEATING OIL
HEAT EXCHANGERS
REACTOR
HEAVY GAS OIL
CATALYST RETURNED TO REGEN. HOPPER
OIL VAPOR
OIL FEED
BOTTOMS
VAPORIZING FURNACES
AIR BLOWER

FIGURE 23

FLUID CATALYST CRACKING PLANT

(Murphree, Brown, Fischer, Gohr, and Sweeney)

(Reprinted by permission from *Ind. Eng. Chem.*, **35**, 771, 1943; courtesy of Standard Oil Development Company.)

$$\underset{\text{di-isobutylene}}{C_8H_{16}\ (\text{liquid})} + H_2 \rightarrow \underset{\text{2,2,4-trimethylpentane}}{C_8H_{18}\ (\text{liquid})}$$

The free energy relation for gaseous isooctane being[5] $\Delta = -28{,}570 + 27.6T$, the vapor reaction is thermodynamically feasible at temperatures below about 750°C. At around 200°C, the reaction is highly exothermic, the free energy change is decidedly negative, and a high partial pressure of hydrogen is not required to effect complete hydrogenation of an octene feed in the presence of a suitable catalyst.

The feed may consist of olefinic materials or mixtures of octenes. The hydrogenation is carried out at a temperature of 180–190°C and a gage pressure of 1 to 4 atmospheres. The catalyst consists of activated nickel supported on porcelain, which is made by impregnating the porcelain with hydrated nickel nitrate and reducing in a current of hydrogen. Sulfur poisons the catalyst, and is removed by a pretreatment of the octene feed with the spent catalyst. Proper treatment of butylenes, before polymerization, reduces the sulfur content of the octene feed to below 0.002 per cent by weight, and a pretreatment with a spent catalyst reduces this figure, on the average, to 0.0005 per cent or less. An octene feed, treated in this manner, contains only enough sulfur to cause slow deactivation of the catalyst. In plant operation, 1,000 gallons of finished isooctane are produced per pound of nickel charged to the catalyst chambers. This average is attained with an average of three reactivations of the catalyst with air in situ, the oxidized catalyst subsequently being reduced by hydrogen. The hydrogen should be free from sulfur and other catalyst poisons, but inert gases, such as nitrogen, methane and carbon dioxide, are not detrimental, whereas carbon monoxide and oxygen induce temporary loss of activity which can be restored by reactivation. In single-stage operation, 10–15 per cent excess of hydrogen is desirable in order to increase the rate of conversion. When, however, the cost of hydrogen is high, a two-stage, counter-current flow system, or direct recycling of residue gas, through a single-stage converter, is used. In a two-stage system, the octene feed to the first converter is mixed with vent hydrogen from a second reactor, which receives fresh hydrogen, together with partially-converted octenes, from the first reactor as feed. In this way, a hydrogen utilization of 95 per cent is readily attained.

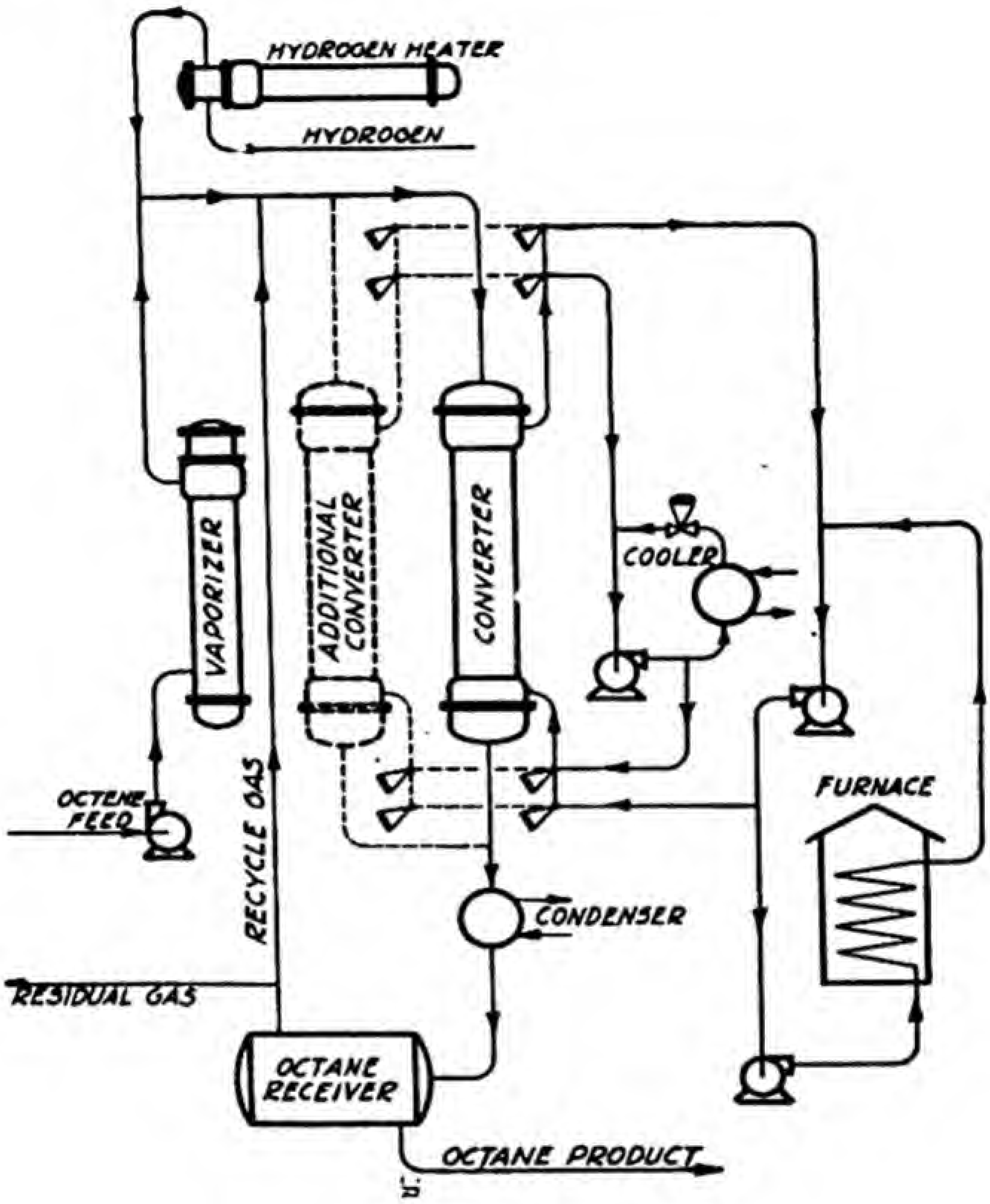

HYDROGEN HEATER
HYDROGEN
VAPORIZER
ADDITIONAL CONVERTER
CONVERTER
COOLER
OCTENE FEED
RECYCLE GAS
FURNACE
CONDENSER
RESIDUAL GAS
OCTANE RECEIVER
OCTANE PRODUCT

FIGURE 24

SINGLE-STAGE SYSTEM

(Courtesy of Shell Development Company, Emeryville, California.)

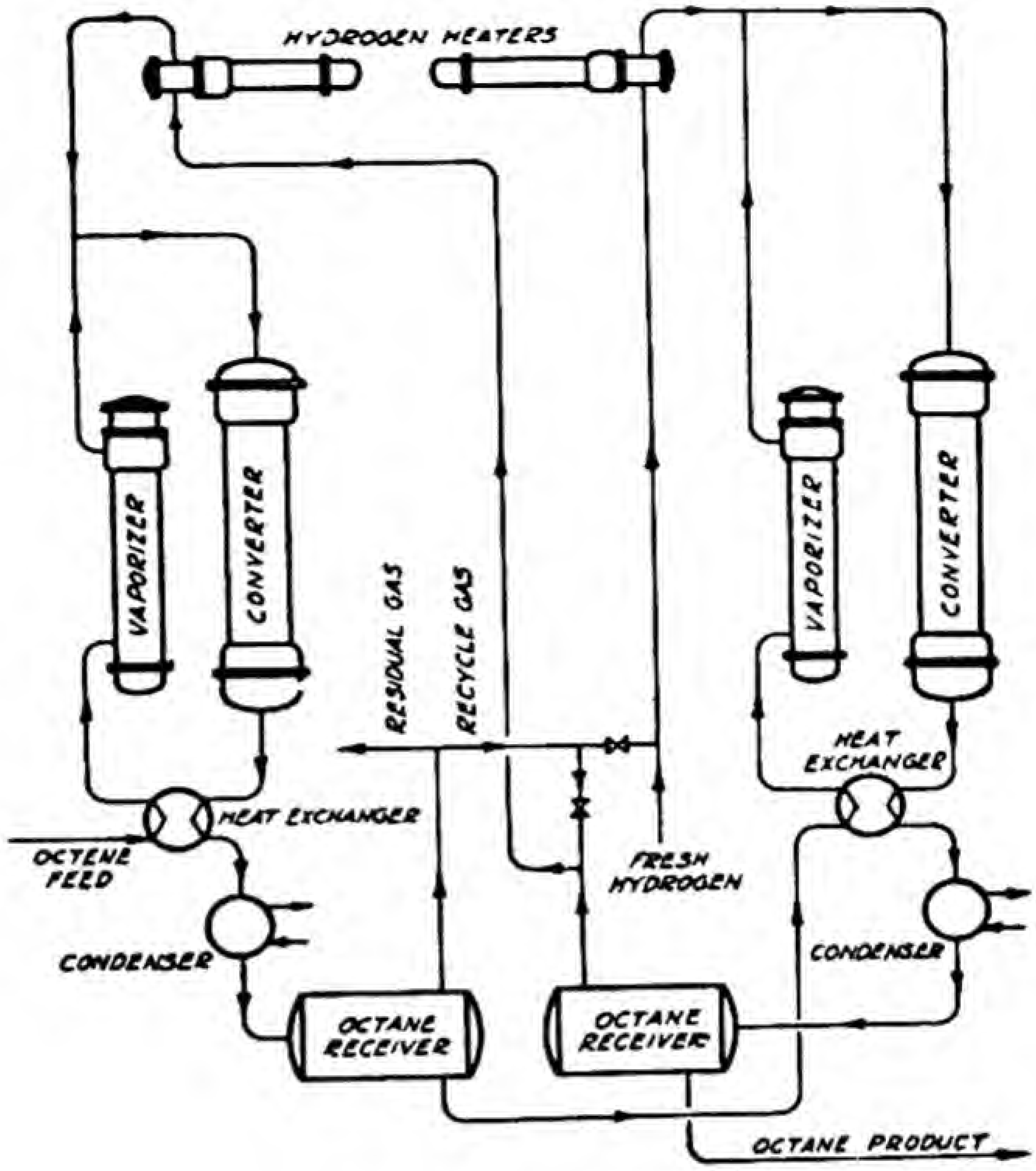

HYDROGEN HEATERS
VAPORIZER
CONVERTER
RESIDUAL GAS
RECYCLE GAS
VAPORIZER
CONVERTER
HEAT EXCHANGER
HEAT EXCHANGER
OCTENE FEED
FRESH HYDROGEN
CONDENSER
CONDENSER
OCTANE RECEIVER
OCTANE RECEIVER
OCTANE PRODUCT

FIGURE 25

TWO-STAGE COUNTERCURRENT SYSTEM

(Courtesy of Shell Development Company, Emeryville, California.)

The properties of the finished octane are as follows:

	Octane from mixed octene fraction	Technical Isooctane
Gravity, °A.P.I.	66.3	70.9
Color, Saybolt	30	30
Reid vapor pressure, lb	2.6	2.1
Unsaturation, per cent by weight	1.1	1.8
Copper-dishgum, mg per 100 ml	1	1
Accelerated gum, mg per 100 ml	1	1
Wright acid heat, °F	26	23
Navy acid heat, °F	7	3
Sulfur (nephelometric) per cent by weight	0.0001	0.001
Octane No., A.S.T.M.	98.2	99.7
A.S.T.M. Distillation, °F, Initial boiling point	196	205
Dry point	236	235

	Octane from mixed octene fraction	Technical Isooctane
10-per-cent point	221	210
30-per-cent point	225	210
50-per-cent point	227	212
80-per-cent point	230	214
90-per-cent point	231	215
95-per-cent point	233	216
Distilled, per cent by volume	99	99

c. *Polymerization Process* (Universal Oil Products Company)[9]

It has been estimated that the world petroleum industry has (1940) an investment of about 20 billion dollars and a production of about two billion barrels of crude annually, of which about eight hundred million barrels of motor fuel are produced. Due to an increasing demand for gasoline, the cracking of petroleum to the lower boiling fractions, used for motor fuel, has progressed to a point where more gasoline is made by cracking than is obtained by distillation of the crude oil.

Besides the resources of petroleum, huge quantities of hydrocarbon gases are available, the figures for the United States, in 1939, being in million cubic feet:

	Natural Gas	Refinery Gas Crude Distillation	Cracked Gas	Total Hydrocarbon Gas
Methane	1,725	152.5	185.5	2,063.0
Ethane	350	52.5	52.5	455.0
Propane	225	30.0	17.5	272.5
Butanes	125	10.0	7.0	142.0
Ethene	—	—	21.0	21.0
Propene	—	—	45.5	45.5
Butenes	—	—	21.0	21.0

The potentialities of ultization of petroleum, as a basis for a very wide range of organic chemical products, are truly great. The petroleum industry realizes this as it appears from the fact that this industry in the United States spends about $20,000,000 annually on research, i.e., about one per cent calculated on the invested capital.

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[9] Berkman, S., J. C. Morrell, and Gustav Egloff: *Catalysis, Inorganic and Organic,* New York, Reinhold Publishing Corporation, 1940, p. 1003.

In converting these lighter hydrocarbon fractions into high-octane motor fuel, catalytic reactions are applied as described below.

The lighter hydrocarbons, occurring in natural gas or petroleum, are paraffinic and not very active. In order to utilize these light fractions, they must be converted into olefins, diolefins and aromatics by pyrolytic catalytic processes.

Higher hydrocarbons serve for the production of ethylene and acetylene. Ethylene (40%) is produced from hydrocarbons at 565–620°C, and atmospheric pressure in less than 0.1 second. The catalytic processes involved in processing the components of the various hydrocarbon mixtures are discussed in the following:

Polymerization of the olefinic hydrocarbons is possible thermally or photochemically, and also catalytically by mineral acids. The polymerization of propene and butene with H_2SO_4 or H_3PO_4 (Ipatieff) can be controlled, the polymerization of ethylene less so.

By catalytic polymerization of the gaseous olefinic hydrocarbons,[9, 10] such as propene and butenes, the yield obtained is practically theoretical at 200°C and 400 lb pressure or higher. Selective polymerization of the normal butenes and isobutenes is carried out at 150°C and 700 lb of pressure.

Hydrocarbons in gas to be polymerized	Temp. °C	Pressure lb	Octane rating	
			Direct	Blending value
Propene, butenes	200	400	80	up to 135
N-butene, isobutenes	150	700	84	over 150
Isobutanes	hydrogenation		95–98 to over 100 for individual octanes	

Anti-knock value of various octanes[9]

n-octane	–28.0
3-methylheptane	34.5
2,5-dimethyl hexane	52.0
2,3-dimethyl hexane	75.5

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[10] Egloff: *Ind. Eng. Chem.*, **28**, 1461 (1936).

3,4-dimethyl hexane	84.5
3-methyl-3-ethylpentane	90.5
2,2,4-trimethylpentane	100.0
2,2,3-trimethylpentane	101.0
2,2,3,3-tetramethylbutane	103.0

The octane numbers of polymer gasolines vary from 80 to 84. The yield of polymer gasoline based on a 10-pound Reid vapor pressure varies between 4 and 9.4 gallons per 1000 cubic feet, depending on the olefin content of the gas. Cracked gas, containing about 40 per cent olefins gives an olefin conversion up to 95 per cent. For gases, low in olefins, the conversion is about 85 per cent or higher.

The polymerization process may be operated non-selectively or selectively. In the latter case, the stock is selected for reaction chiefly between isobutene and butenes to produce 90 to 95 per cent of isooctenes, with some heavier polymers, the octane numbers varying between 95 and 97 after hydrogenation of the isooctenes to isooctanes.

Hydrogenation. The isooctenes are converted into isooctanes at 160°C and 75 lb pressure (Universal Oil Process), using a nickel catalyst, this process being exothermic. The isooctanes are blended with aviation stock.

Isomerization. The most important process is the direct alkylation of isobutane with butenes to produce isooctane, the isobutane being made by conversion of n-butane. Direct isomerization of n-butane to isobutane (66.5%) takes place in the presence of dry $AlCl_3$ (16.4%) and dry HCl, by heating for 12 hours at 150°C temperature and 30 atm. pressure.[9, 11]

Cracking. This process applies to the partially-controlled decomposition of heavier oil to make lighter ones, the means of operation being elevated temperatures and pressures and suitable catalysts.[9] A cracked gas analysis is the following:

	%		%
H_2	15.9	C_3H_8	5.8
CH_4	18.5	iso-C_4H_8	8.8

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[11] Egloff, Morrell, Thomas, and Bloch: *J. Am. Chem. Soc.*, **61**, 3571 (1939).

C_2H_4	4.8	n-C_4H_8	12.3
C_2H_6	5.2	C_4H_{10}	5.0
C_3H_6	21.5	O_2	0.3
		CO	0.6
		N_2	2.0

The catalyst used is of the alumina-silica type.[11]

In the Houdry cracking process, activated hydrosilicate of alumina is used as catalyst. This catalyst has a long life. A 45 per cent yield of high-octane gasoline, having an octane number of 77 to 81, is obtained per pass.

Reforming[9] is the process of converting lower-boiling distillates (gasoline, naphtha) into products of higher anti-knock value, i.e., higher octane rating. This treatment is generally accomplished by catalytic or thermal processes. The oil is heated to 430–450°C, the vapors passing into a catalyst chamber, and from there into a fractionating column. Carbon deposits on the catalyst, which is regenerated by burning the carbon off. Two catalyst chambers are used so that one is converting while the other is regenerating. Regeneration takes about half an hour. Granules or pellets of silica-alumina or alumina-chromia, in a stationary bed, in chambers or tubes, are used as catalysts. The octane value of the resulting gasoline is about 80, the conversion being 80–90 per cent. The finished product is formed by conversion of paraffin hydrocarbons to aromatics and isomerization to isoparaffins, and it is said in general to constitute a satisfactory motor or aviation gasoline.

Dehydrogenation.[12] In conversion of paraffinic hydrocarbons to the corresponding olefins, under heat and pressure, oxides of the transition metals of the 4th, 5th and 6th groups of the periodic system, on suitable supports, e.g., alumina, are used as catalysts. Catalysts made from chromium oxide on alumina have a long life, are highly selective, and convert the paraffins into olefins with a yield of 90 to 95 per cent. The yield of H_2 is about 90 per cent. Only 1 atm. pressure and 500–700°C temperature are used, the space velocity varying from 500 to 10,000 or higher.

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[12] **Grosse and Ipatieff:** ***Ind. Eng. Chem.*, 32, 268 (1940).**

The Shell Development Co., who are pioneers in the field of dehydrogenation, use activated alumina promoted by chromium-oxide and a small amount of water (monomolecular layer), as this reaction does not take place under absolutely dry conditions.

The products, resulting from dehydrogenation, are chiefly: n-butenes and isobutenes, unconverted butanes, H_2, and small quantities of methane, ethane and ethene, propane and propene. The gases are compressed, cooled, and passed to a separator where the gaseous and liquid fractions are withdrawn.

Combined dehydrogenation—polymerization—hydrogenation.[9] This process is used for production of isooctane (Universal Oil Products Co. process), and aviation fuel from mixtures of isobutane and normal butane. The butanes are preheated to approximately 580°C and dehydrogenated over chromium oxide on alumina in vertical tubes where approximately 25 per cent of the charge is converted, the gases leaving the tubes at a pressure only slightly above 1 atm. and at a temperature of about 610°C. The butane-butene mixture is cooled and compressed to 100–200 lb, the H_2 is separated, the butane-butene being polymerized under high pressure using U.O.P.H_3PO_4-catalyst (temperature: 120–180°C; pressure: 750–1500 lb). The polymer is debutanized, distilled, and catalytically dehydrogenated to endpoint aviation gasoline of approximately 97 octane number. The hydrogen, for the hydrogenation, is obtained by the dehydrogenation; nickel is used as catalyst. The hydrogenation pressure is about 35 lb and the temperature 180°C. The hydrogenated product consists essentially of isooctanes.

Gas cracking and polymerization,[9] in combination, are operated commercially. The cracked gas is polymerized. Typical charging stock for the cracking—catalytic polymerization showed the following analysis in mol per cent:

Propane	3.3
n-Butane	83.2
Isobutane	12.2
Pentane	1.3

This charging stock was heated to a temperature of 575°C at 750 lb pressure in the cracking unit. The resulting pyrolytic polymer gasoline was of the following quality:

Gravity (°A.P.I.)	48.5
100 cc Distillation (A.S.T.M.)	
I.B.P. (°F)	119
Per cent distilled over	
10	147
20	159
50	202
—	—
90	407
E.P. (°F)	520
Octane No. (C.F.R. Method)	74
Reid Vapor pressure (lb)	4.7
Sulfur (%)	0.22

Catalytic alkylation[13, 14, 15, 16] of hydrocarbons has assumed great industrial importance as it serves as a process for production of high-octane aviation fuel. For this purpose, branched-chain paraffins are used. In this way, it is possible to utilize the highly volatile gaseous hydrocarbons, e.g., those containing three or four carbon atoms, for making motor fuel, which otherwise would not be suitable for use because of their high volatility.

Sulfuric acid has proved to be a commercially suitable catalyst for the alkylation of the lower paraffins. Experience has shown that this cheap catalyst provides for a process which can be handled in standard engineering equipment on a large scale, and by which a superior aviation fuel can be produced. The sulfuric acid process was developed jointly by the Anglo-Iranian Oil Co. Ltd., Humble

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[13] *High-Octane Aviation Fuel by the Sulfuric Acid Alkylation Process*, paper presented to the Group Session on Alkylation and Catalysis, under the auspices of the Division of Refining, at the 20th Annual Meeting of the Am. Petroleum Inst., November 17, 1939, by S. H. McAllister, Shell Development Company.

[14] Malishev: *J. Am. Chem. Soc.*, **57**, 883 (1935).

[15] *The Catalytic Hydrogenation of Octenes to Octanes*, a contribution of the combined staffs of the Shell Development Company and Shell Chemical Company, paper for presentation at 8th Mid-Year Meeting of Am. Petroleum Inst., May 24, 1938.

[16] McAllister, Anderson, Ballard, and Ross: *J. Org. Chem.*, **6**, 647 (1941).

Oil and Refining Co., Shell Development Co., Standard Oil Development Co., and The Texas Co. research staffs.[1]

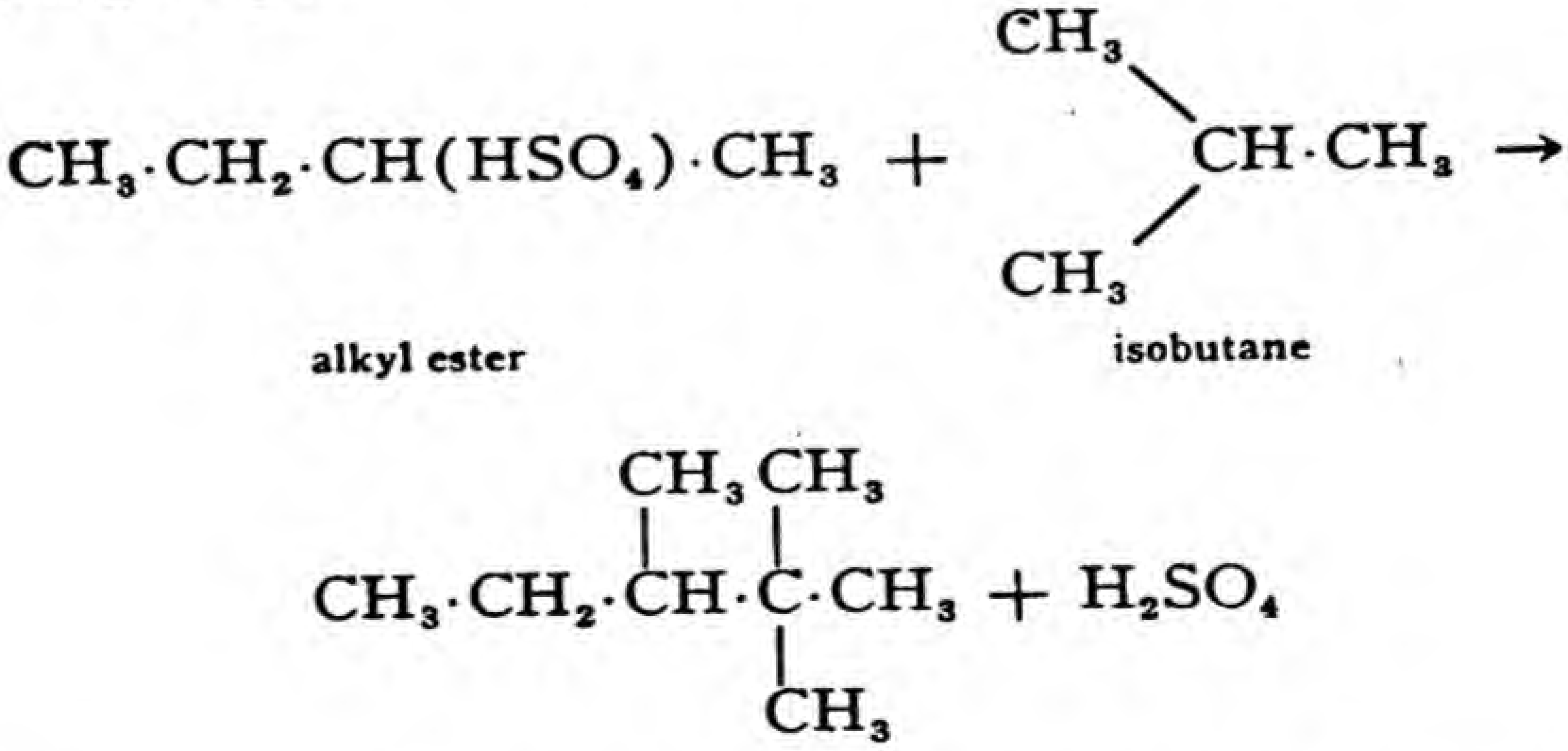
When aliphatic olefins are mixed with strong sulfuric acid at around room temperatures, the primary reaction is one of olefin absorption in the acid to form alkyl sulfates. This absorption is a relatively rapid exothermic reaction. Saturated normal hydrocarbons remain virtually unabsorbed, but isoparaffins, such as isobutane, are absorbed, to a slight extent, if the sulfuric acid concentration is 90 per cent or higher. It has been estimated that the rate of absorption of olefins is about 700 times faster than that of the isoparaffins.

The coupling reaction occurs in the acid phase through the formation of an olefin acid ester, which then reacts with the isobutane, the reaction, in its simplest form, consisting of two steps, but, in fact, being more complicated than it will appear from the following scheme:

1. Absorption step:

$$\underset{\text{butylene-1}}{CH_3{\cdot}CH_2{\cdot}CH{=}CH_2} + H_2SO_4 \rightarrow \underset{\text{alkyl ester}}{CH_3{\cdot}CH_2{\cdot}CH(HSO_4){\cdot}CH_3}$$

2. Coupling step:



In order to prevent the absorption step from proceeding to a point where the acid becomes useless for coupling, it is desirable to have present in the reaction zone a vast excess of isoparaffin.

Sulfuric acid is the only chemical agent used, although a caustic wash of the product usually is provided to neutralize any traces of acid which might be carried over from the separator to the fractionation system. As to operating details, reference is made to the original papers.

Alkylation can be carried out with a wide variety of olefins and isoparaffins, but for all practical purposes olefins containing C_3–C_8, inclusive, and from the isoparaffins, isobutane and isopentane, are used. Ethylene-containing feed stocks may be used, but the reaction is accompanied by an increased acid consumption. Olefins above C_8 yield products boiling largely above the aviation-gasoline range, but it has been found that some C_4 and C_3 polymers, containing eight or more carbon atoms, prepared by catalytic processing, and some other olefins of branched structure rearrange, on alkylation, to yield products boiling below the temperatures expected and predominantly in the gasoline range.

Isobutane is the most widely-used isoparaffin in alkylation, since, on account of its high volatility, it has restricted use in gasoline. When coupled with olefins, it leads to products having a highly-branched structure. Isopentane and isohexane are, in themselves, valuable constituents of gasoline, and would be used only in the alkylation process if large quantities were available over and above those required to meet volatility requirements.

Isobutane is alkylated readily by most of the pure olefins, and with low catalyst consumption. Unfortunately, in the refinery, the olefins are present in mixtures along with dienes, aromatics, mercaptans, thiophenes, and other substances. These may affect markedly the yield and acid consumption, as in the laboratory, it has been shown that mercaptans, amines, dienes, aromatics, and oxygenated compounds are absorbed by the acid, and reduce its activity rapidly.

The cost of pretreating the feed, to remove these impurities, must be weighed against the resulting economy in acid. For example, the oxidation of the sulfur compounds causes an increase in consumption of acid, but does not affect directly the quality of the product. Therefore, a simple caustic wash is recommended. Amines, if present, can be removed by water washing. Dienes (butadiene will alkylate to give principally octanes, but the acid consumption is high), aromatics, and oxygenated compounds, however, are more difficult to remove, and it is doubtful if a pretreatment would be worth while.

Entrained water is removed by settling, but the quantity of dissolved water present would hardly justfy the expense of predrying the feed. Thus, each feed stock constitutes a separate problem depending on the amount and type of impurity present, and may require adjustment of the operating conditions over and above the adjustments necessary when operating with olefins of different purity.

The properties of products, from alkylation with representative olefin feed stocks were as listed on p. 381.

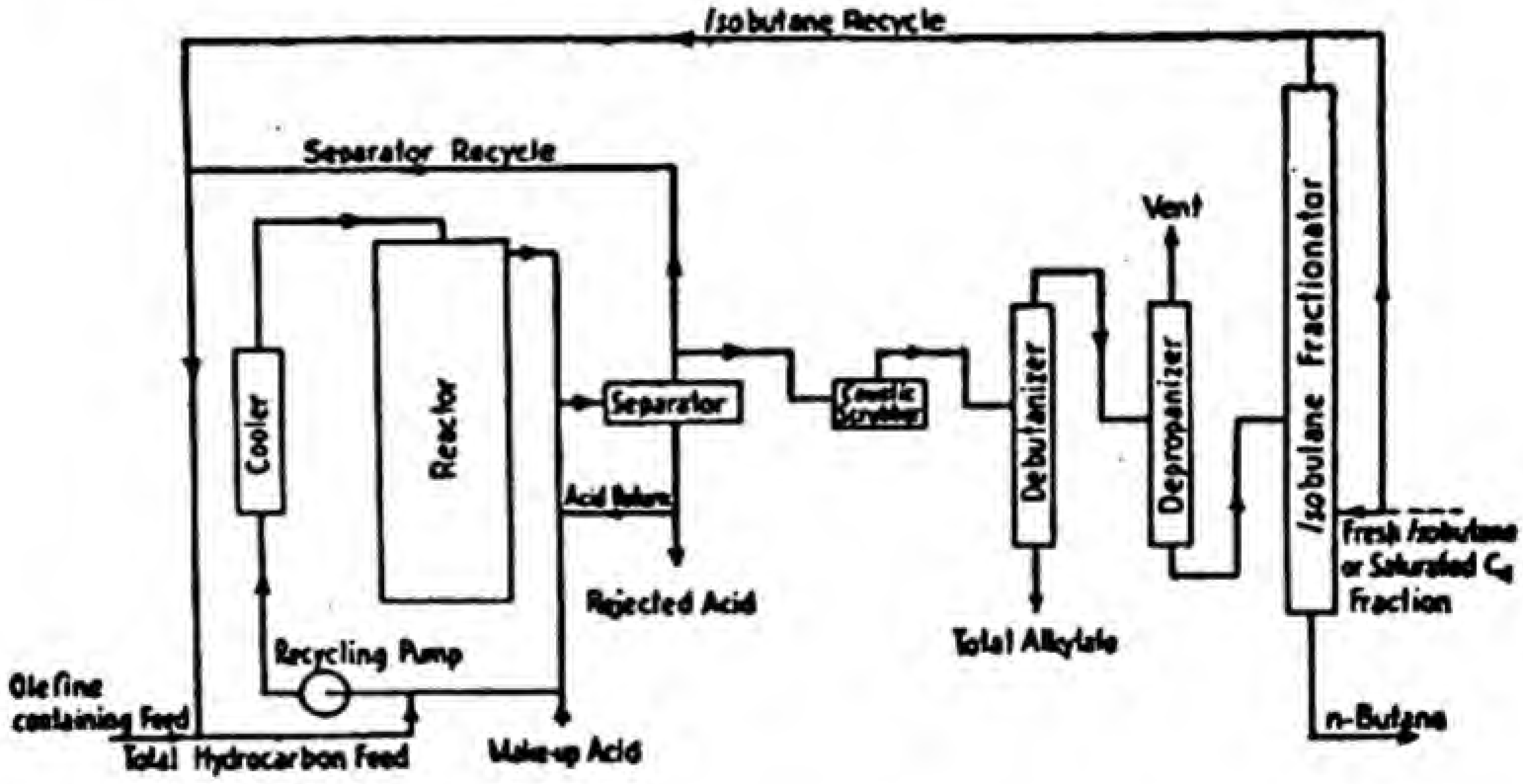

Isobutane Recycle
Separator Recycle
Vent
Cooler
Reactor
Separator
Caustic Scrubber
Debutanizer
Depropanizer
Isobutane Fractionator
Acid Return
Rejected Acid
Total Alkylate
Fresh Isobutane or Saturated C_4 Fraction
Recycling Pump
Olefine containing Feed
Total Hydrocarbon Feed
Make-up Acid
n-Butane

FIGURE 26

FLOW DIAGRAM OF SULFURIC-ACID ALKYLATION PLANT

(Courtesy Shell Development Company, Emeryville, California.)

Alkylation with Representative Refinery Olefin Feed Stocks[13]

Olefin Feed Stock (Per Cent by Weight of Olefin)	C_3 Fraction from Cracking 30[a]	C_4 Fraction from Cracking 48[b]	Residual C_4 Fraction from *Iso*octane Manufacture 24[c]	C_5 Fraction from Cracking 55	70- to 160-°F End-Point Cracked Gasoline 52	70- to 210-°F End-Point Cracked Gasoline 50
Conditions:						
*Iso*paraffin used	*Iso*butane	*Iso*butane	*Iso*butane	*Iso*butane	*Iso*butane	*Iso*butane
Mole ratio of *iso*paraffin to olefin	8	5	5	8	8	8
Makeup acid strength, per cent by weight of sulfuric acid	98–100	98–100	98–100	98–100	98–100	98–100
Volume ratio of acid to hydrocarbon ratio	1	1	1	1	1	1
Temperature, °F	85	32–50	32–50	50	50	50
Contact time, min	20–40	20–40	20–40	20–40	20–40	20–40
Titratable acidity of rejected acid, as per cent by weight of sulfuric acid	88–90	88–90	88–90	88–90	88–90	88–90
Per cent by weight of yield of total alkylate based on olefin in feed	185	190–200	200–215	134[d]	126[d]	115[d]
Per cent by volume of total alkylate based on olefin in feed	138	158–166	168–180	125[d]	119[d]	113[d]
Aviation fraction (end point, 300 °F) in total alkylate, per cent	92–95	88–90	89–91	90	85	77
Makeup acid, lb per gal of total alkylate	2.6	1	<1	1.5	1.7	3.3

[a] With mixed C_3 and C_4 fractions, materially better results are obtained.

[b] About 18 per cent isobutylene present.

[c] Largely butylene-2.

[d] Yield based on total refinery fraction, which includes saturates.

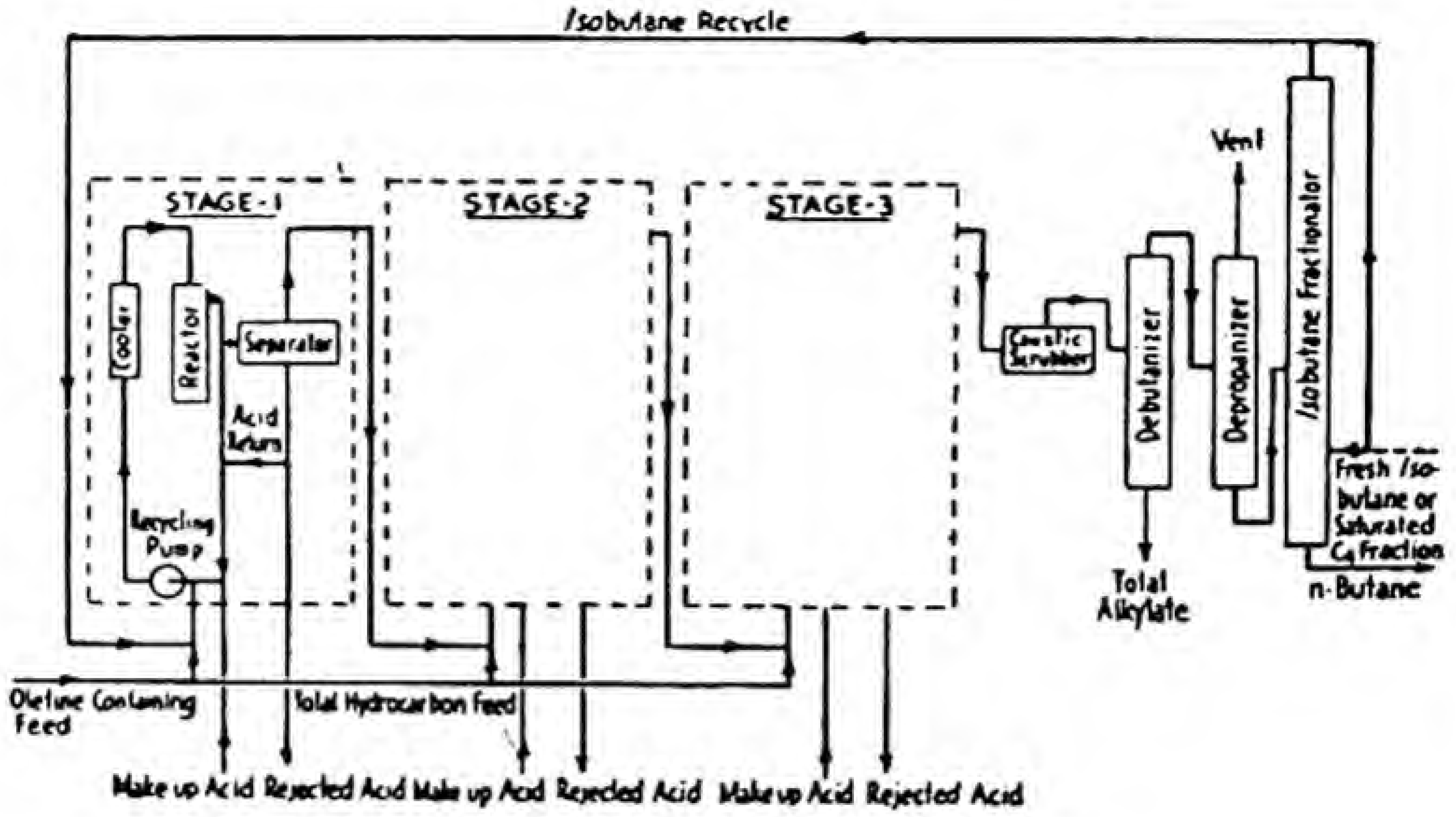

Isobutane Recycle
STAGE-1
STAGE-2
STAGE-3
Cooler
Reactor
Separator
Acid Return
Recycling Pump
Caustic Scrubber
Debutanizer
Depropanizer
Isobutane Fractionator
Vent
Total Alkylate
Fresh Isobutane or Saturated C_4 Fraction
n-Butane
Olefine Containing Feed
Total Hydrocarbon Feed
Make up Acid
Rejected Acid
Make up Acid
Rejected Acid
Make up Acid
Rejected Acid

FIGURE 27

FLOW DIAGRAM OF THREE-STAGE SULFURIC-ACID ALKYLATION PLANT, SPLIT-OLEFIN FEED[13]

(Courtesy Shell Development Company, Emeryville, California.)

This work is very important and noteworthy, because it is not only a great accomplishment in chemical research, resulting in the production of high-quality aviation fuel when it is vitally needed, but it also shows what coordinated and cooperative research can accomplish.

Finally, attention should be called to the Triptane process by which 2,2,3-trimethylbutane is made catalytically. This compound is the most suitable hydrocarbon for use in internal combustion engines, and together with two other hydrocarbons, made in the same conversion (2,3-dimethylbutane, and 2,3-dimethylpentane), it is used in aviation blends. The details of the processes involved in making this aviation fuel are, at this time, a military secret.[18]

GENERAL REFERENCES

Institution of Automotive Engineers, Australia: *Modern Eng.*, July 20, 1941; Egloff, Hulla, and Komarewsky: *Isomerization of Pure Hydrocarbons*, Am. Chem. Soc. Monograph, New York, Reinhold Publishing Corp., 1942.

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[18] Haensel and Ipatieff: *Science*, **98**, 495 (1943).

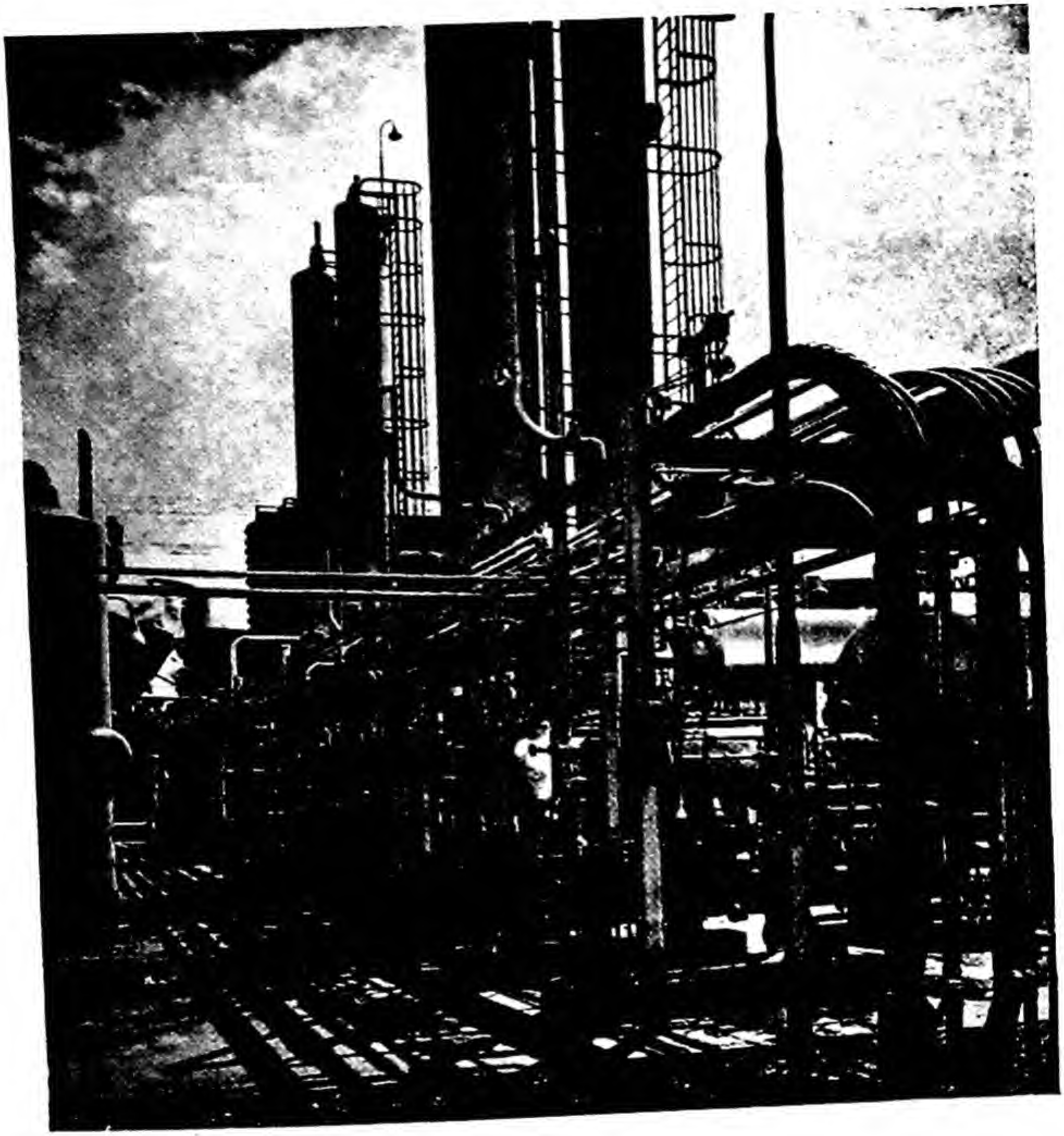

FIGURE 28

MARTINEZ ALKYLATION PLANT OF SHELL OIL COMPANY[13]

(Courtesy of Shell Development Company, Emeryville, California.)

8. Synthetic rubber

Natural rubber is a polymer of isoprene, $(C_5H_8)n$, although it also contains accessory amounts of resins, proteins, and minerals which are precipitated with the rubber from rubber latex. The rubber fraction is soluble in carbon disulfide, benzene, chloroform, and other rubber solvents.

When distilled, dry natural rubber yields isoprene, C_5H_8, the constitution of which was confirmed by Tilden[1] to be 2-methylbutadiene $CH_2{=}C(CH_3) \cdot CH{=}CH_2$. The fact that isoprene is the mother substance of natural rubber was early recognized by Williams[2] and Bouchardat[3] who showed that isoprene can be polymerized to a product having the characteristics of rubber, the reaction being brought about by heating isoprene with fuming hydrochloric acid. Thiele[4] found that piperylene (1-methyl butadiene), $(CH_3)CH{=}CH \cdot CH{=}CH_2$, polymerized to a rubber-like substance; and Kondakoff[5] found that the same was true of 2,3-dimethyl butadiene, $CH_2{=}C(CH_3) \cdot C(CH_3){=}CH_2$, when heated with alcoholic potash. Butadiene, $CH_2{=}CH \cdot CH{=}CH_2$, a gas, polymerizes to rubber upon heating (Lebedev,[6] Harries[7]).

Whitby and Gallay[8] studied the polymerization (by heating for 30 days at 100°C, and for 15 days at 150°C) of di-, tri-, and tetramethylbutadienes and found that the higher the degree of substitution of the butadienes, the less readily does polymerization occur. Furthermore, the presence of unsubstituted terminal hydrogen atoms is favorable to polymerization. 2,3- and 1,3-dimethylbutadiene only give a definite rubber-like product, 1,2-dimethylbutadiene gives a gelatinous product, and substituted butadienes, containing more than two methyl groups, give, at best, low, oily polymers having no rubber-like character.

The extensive research, carried out in order to solve the problem of making synthetic rubber, has been directed toward preparation of dienes (butadiene, isoprene, and 2,3-dimethylbutadiene) from suitable raw materials, such as coal tar, starch, petroleum, and hydrocarbon gases, and polymerization of the dienes.

Ostromislensky[9] passed alcohol, with a little air, over heated copper gauze so that the alcohol was partly oxidized to acetaldehyde. This mixture was then passed over heated alumina at 360 to 340°C, yielding water and about 25% by weight of butadiene.

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[1] Tilden: *Chem. News*, **46**, 120 (1882); *J. Chem. Soc.*, **45**, 410 (1884).

[2] Williams: *Proc. Roy. Soc. (London)*, **10**, 516 (1860).

[3] Bouchardat: *Compt. rend.*, **80**, 1446 (1875); *ibid.*, **89**, 1117 (1879).

[4] Thiele: *Liebigs Ann. Chem.*, **308**, 337 (1899).

[5] Kondakoff: *J. prakt. Chem.*, **62**, 172 (1900).

[6] Lebedev: *J. Russ. Phys. Chem. Soc.*, **42**, 949 (1910).

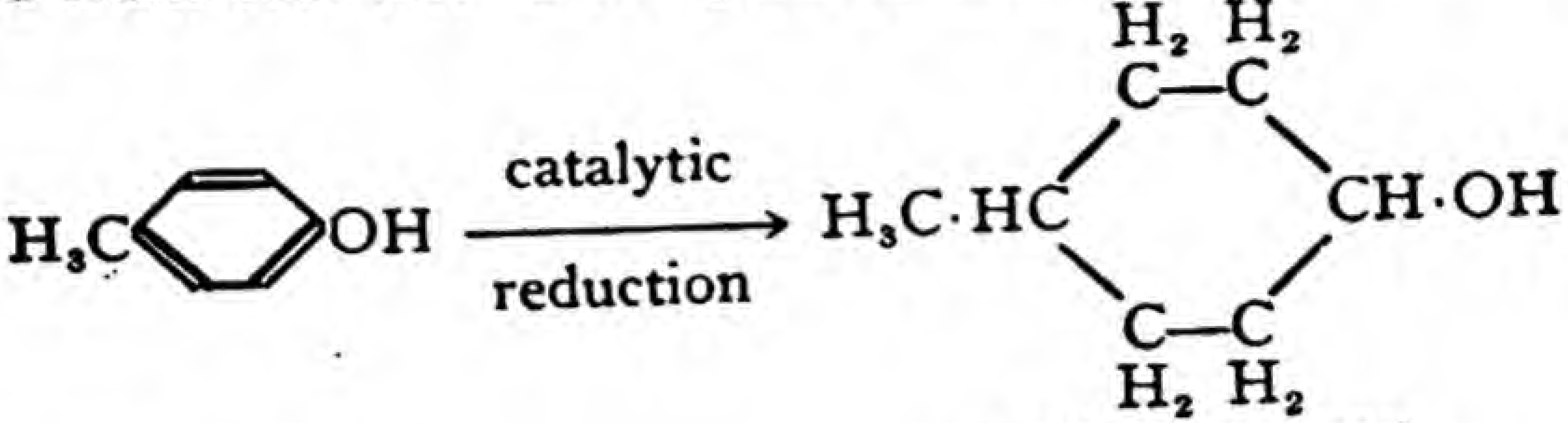
[7] Harries: *Liebigs Ann. Chem.*, **383**, 157 (1911); *Ber.* **47**, 1999 (1914).

[8] Whitby and Gallay: *Can. J. Research*, **6**, 280 (1932).

[9] Ostromislensky: *J. Soc. Chem. Ind.*, **35**, 70 (1916).

$$CH_3 \cdot CHO + CH_3CH_2OH \rightarrow CH_2{=}CH \cdot CH{=}CH_2 + 2H_2O$$

Hofmann and Coutelle[10] made isoprene from cresol or phenol derived from coal tar. Their process was carried out as follows:



p-cresol

p-methyl-cyclohexanol

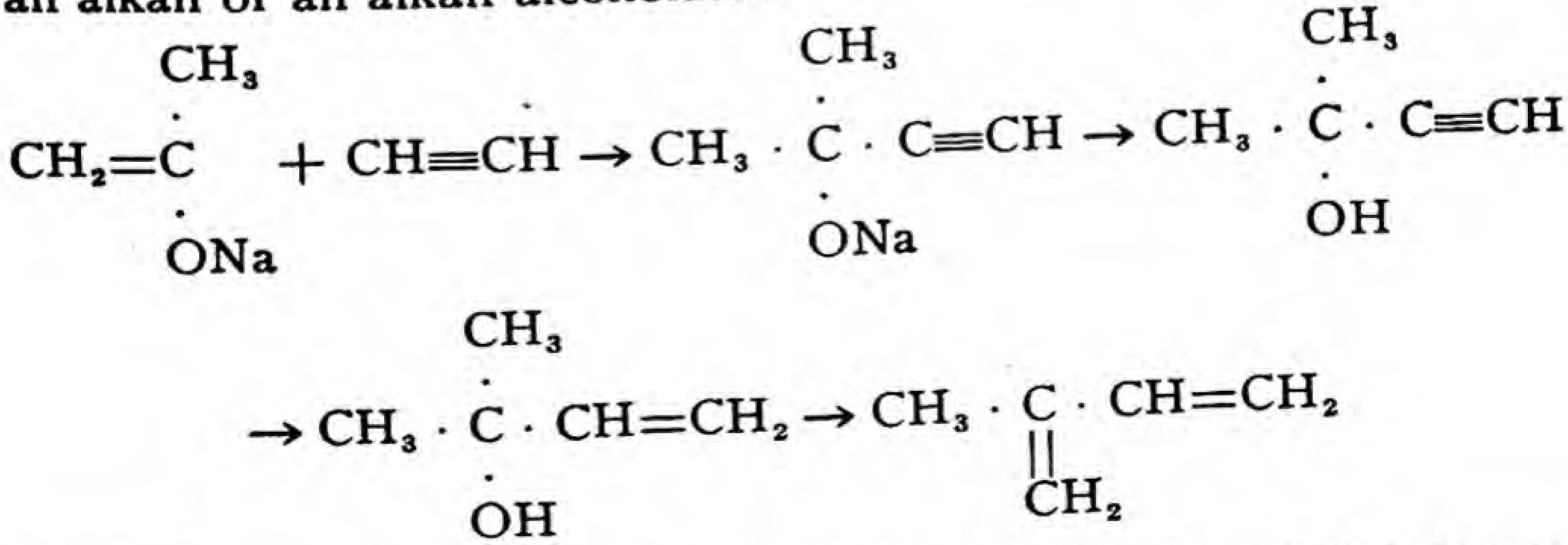
$$\xrightarrow{\text{oxidation by } HNO_3} \underset{\beta\text{-methyladipic acid}}{HOOC \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot COOH}$$

$$\longrightarrow \underset{\beta\text{-methyladipic amide}}{NH_2 \cdot OC \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot COOH}$$

$$\longrightarrow \underset{\beta\text{-methyltetramethylene diamine}}{NH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot NH_2}$$

$$\longrightarrow \underset{\text{isoprene}}{CH_2{=}C(CH_3) \cdot CH{=}CH_2}$$

It is claimed that Merling,[11] prior to World War I, succeeded in making isoprene from acetylene and acetone in the presence of an alkali or an alkali alcoholate:



$$CH_2{=}\overset{\overset{\displaystyle CH_3}{\cdot}}{\underset{\underset{\displaystyle ONa}{\cdot}}{C}} + CH{\equiv}CH \rightarrow CH_3 \cdot \overset{\overset{\displaystyle CH_3}{\cdot}}{\underset{\underset{\displaystyle ONa}{\cdot}}{C}} \cdot C{\equiv}CH \rightarrow CH_3 \cdot \overset{\overset{\displaystyle CH_3}{\cdot}}{\underset{\underset{\displaystyle OH}{\cdot}}{C}} \cdot C{\equiv}CH$$

$$\rightarrow CH_3 \cdot \overset{\overset{\displaystyle CH_3}{\cdot}}{\underset{\underset{\displaystyle OH}{\cdot}}{C}} \cdot CH{=}CH_2 \rightarrow CH_3 \cdot \underset{\underset{\displaystyle CH_2}{\|}}{C} \cdot CH{=}CH_2$$

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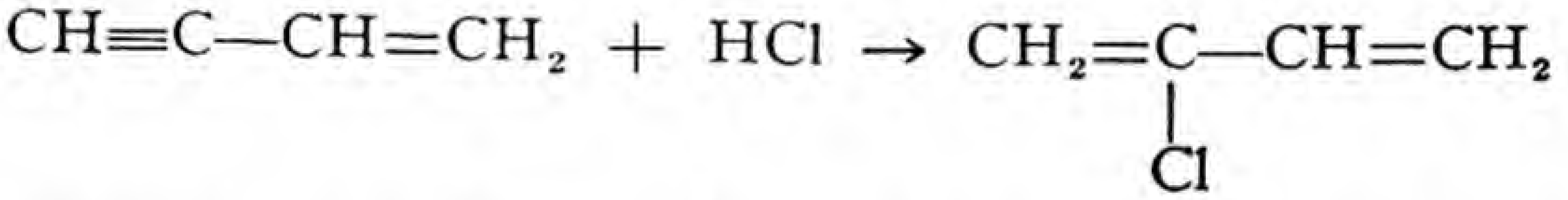
[10] Hofmann and Coutelle: German Patent 231,806 (1909); British Patents 8100 (1910); 17,414, 18,935 and 19,919 (1911).

[11] Vogel and Schulze: *Carbid und Acetylen*, Leipzig, Otto Spamer, 1911.

Using cuprous chloride as a catalyst, preferably with ammonium chloride, acetylene is polymerized to vinyl acetylene,[12] $CH_2{=}CH{\cdot}C{\equiv}CH$ (b.p. 5°C), and divinyl acetylene, $CH_2{=}CH{-}{\cdot}C{\equiv}CH{=}CH_2$ (b.p. 85°C). The chemistry of these compounds has been studied extensively by Carothers and his associates,[13] the result of this study being the discovery of 2-chloro-,1,3-butadiene, $CH_2{=}CCl{\cdot}CH{=}CH_2$, which is known under the name of chloroprene. This compound polymerizes far more readily than does isoprene, the polymerization process being activated by the presence of the chlorine atom. The polymerized product has similar elastic properties to vulcanized natural rubber. Several polymers of different qualities are obtainable.

Chloroprene is prepared by the addition of HCl to vinylacetyléne:[13]



$$CH{\equiv}C{-}CH{=}CH_2 + HCl \rightarrow CH_2{=}\underset{\substack{|\\Cl}}{C}{-}CH{=}CH_2$$

Chloroprene is readily emulsified into a suspension similar to latex by stirring it with water containing an emulsifying agent, such as sodium oleate. When the moisture is removed from a film of this latex, a thin, coherent, strong, elastic film remains. Chloroprene rubbers are marketed under the trade-name of Neoprene.[14]

A variety of polymerization catalysts may be used for polymerizing the monomers,[12, 15, 16] and reference sources should be studied for specific cases. Mineral acids, clays, halides, alkali metals, oxidizing agents, etc., are examples of catalysts used in polymerization of the unsaturated rubber hydrocarbons described here.

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[12] Mark and Whitby: *Collected Papers of Wallace H. Carothers on Polymerization*, New York, Interscience Publishers Inc., 1940.

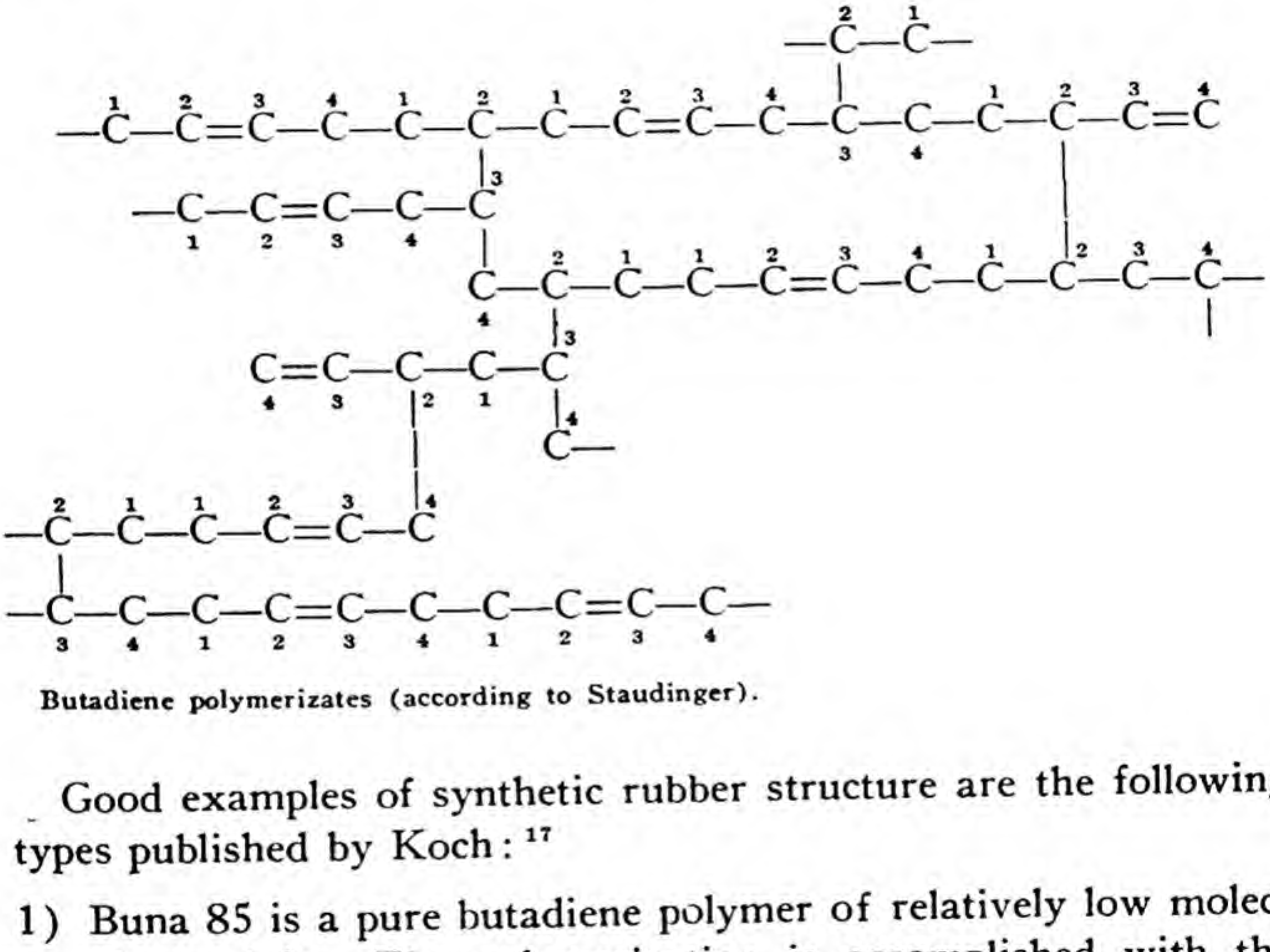
[13] Carothers, Williams, Collins, and Kirby: *J. Am. Chem. Soc.*, **53**, 4203 (1931).

[14] Bridgewater: *Ind. Eng. Chem.*, **32**, 1155 (1940).

[15] Burke, R. E.: *Catalysis in Polymerization*, Twelfth Report of the Committee on Catalysis, National Research Council, New York, John Wiley and Sons, Inc., 1940.

[16] Carothers: *Ind. Eng. Chem.*, **26**, 30 (1934).

In natural rubber, there are approximately 2000 isoprene molecules linked together providing for a molecular weight of 136,000.[17] When butadiene polymerizes the following additions take place: 1–4, 2–3, and 3–4:



Butadiene polymerizates (according to Staudinger).

Good examples of synthetic rubber structure are the following types published by Koch:[17]

1) Buna 85 is a pure butadiene polymer of relatively low molecular weight. The polymerization is accomplished with the help of sodium metal. From this type of product, the name "Buna" originates, since it is a combination of bu for butadiene and na for natrium (sodium).
2) Buna S is a mixed polymer of butadiene and styrene. The polymerization is accomplished in aqueous emulsion.
3) Perbunan is a mixed polymer of butadiene and acrylic nitrile. The polymerization takes place in aqueous emulsion.

---

[17] Koch: *Ind. Eng. Chem.*, **32**, 464 (1940).

The Buna rubbers are synthesized from acetylene as follows:

Acetylene
↓
Acetaldehyde
↓
Acetaldol
↓
Buteneglycol
↓
Butadiene
↓
Rubber polymers

The chemical formulas are described to be as shown on p. 389:[17]

Berkman, Morrell and Egloff[18] state that 160,000,000,000 pounds of butadiene are potentially available from natural gas and refinery gases in the United States. A similar quantity of styrene could be made from ethylene and benzene both derived from petroleum by catalytic processes. A mixture of butadiene and styrene gives a rubber such as Buna S, the wear and strength of which in tires are about 30 per cent better than those of natural rubber. In other words, from such a mix, 320,000,000,000 pounds of synthetic rubber could be obtained annually in the United States. The natural rubber requirements for 1940 were 1,200,000,000 pounds.

Butadiene can be derived from butenes, isoprene from pentenes, and acetylene from methane, in this way, both natural and cracked gases can be used for the production of synthetic rubber, the basic raw materials being natural gas, petroleum, coal, and lignite. Ethyl alcohol, one of the cheapest organic chemicals, can be used as a source for making butadiene, and it is used as such in Russia. Butadiene is also being made from grain. The manufacture of large quantities, from this source, is planned.[19]

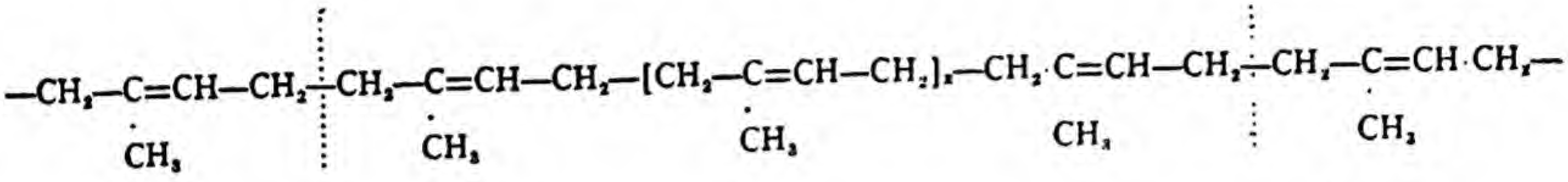
During the last few years, the making of synthetic rubber has

---

[18] Berkman, Morrell, and Egloff: *Catalysis, Inorganic and Organic,* New York, Reinhold Publishing Corp., 1940.

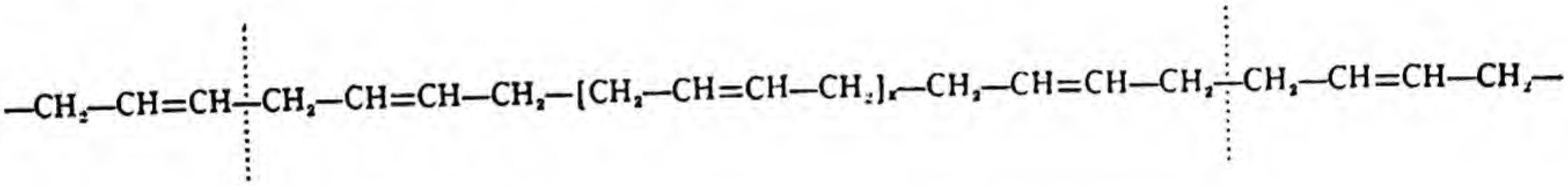
[19] The Synthetic Program, extracted from the Report of the Baruch Committee to the President of the United States, *Ind. Eng. Chem.,* **34,** 1256 (1942).

Natural rubber:



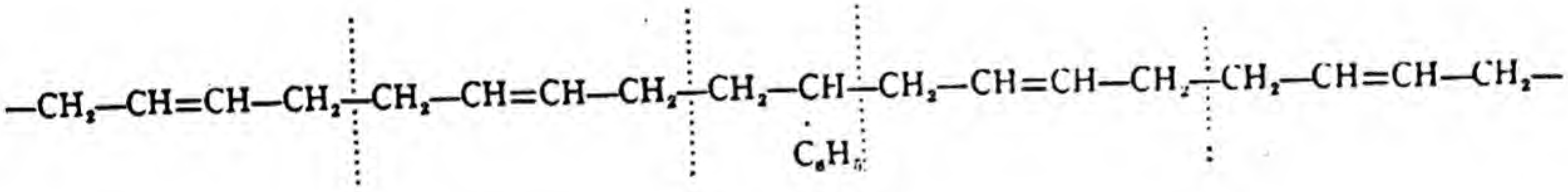
$$-CH_2-\underset{CH_3}{C}=CH-CH_2\vdots CH_2-\underset{CH_3}{C}=CH-CH_2-[CH_2-\underset{CH_3}{C}=CH-CH_2]_x-CH_2\cdot\underset{CH_3}{C}=CH-CH_2\vdots CH_2-\underset{CH_3}{C}=CH\cdot CH_2-$$

Numbered Bunas.



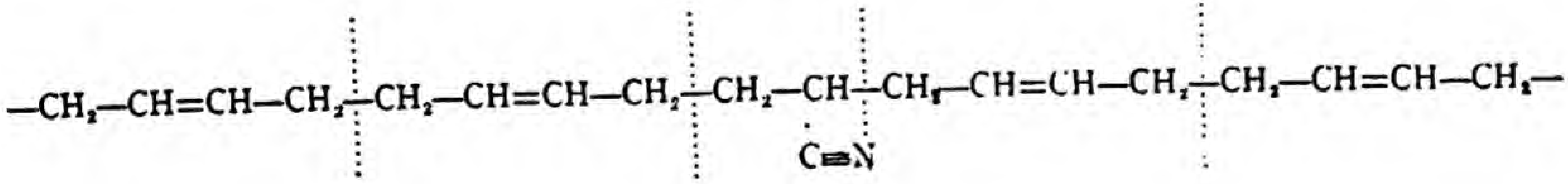
$$-CH_2-CH=CH\vdots CH_2-CH=CH-CH_2-[CH_2-CH=CH-CH_2]_x-CH_2-CH=CH-CH_2\vdots CH_2-CH=CH-CH_2-$$

Buna S:



$$-CH_2-CH=CH-CH_2\vdots CH_2-CH=CH-CH_2\vdots CH_2-\underset{C_6H_5}{CH}\vdots CH_2-CH=CH-CH_2\vdots CH_2-CH=CH-CH_2-$$

Perbunan:



$$-CH_2-CH=CH-CH_2\vdots CH_2-CH=CH-CH_2\vdots CH_2-\underset{C\equiv N}{CH}\vdots CH_2-CH=CH-CH_2\vdots CH_2-CH=CH-CH_2-$$

advanced to a stage of development which few, if any, would have predicted five years or a decade ago.

Besides the history of synthetic rubber by Whitby and Katz[20] in 1933, the progress in manufacture of synthetic rubber has been discussed in a symposium, 1939,[21] a general paper by Cramer,[22] 1942; a comprehensive symposium again in 1942,[23] and papers by Fisher, Murphy and others.[24, 25]

Fisher,[24] in discussing the use of coal in the manufacture of synthetic rubbers, has published some very useful tabulations which are reproduced here, and which give a brief and lucid illustration of a long story.

---

[20] Whitby and Katz: *Ind. Eng. Chem.*, **25**, 1204 (1933). Detailed summary of the history of the development of synthetic rubber.

[21] Symposium. *Ind. Eng. Chem.*, **31**, 934 (1939).

[22] Cramer: *Ibid.*, **34**, 243 (1942).

[23] Symposium. *Ibid.*, **34**, 1253 (1942).

[24] Fisher: *Ibid.*, **34**, 1382 (1942).

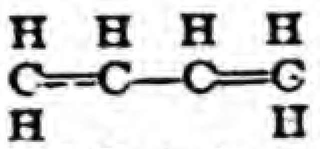
[25] Production of synthetic rubber. Fisher: *Chem. Eng. News*, **21**, 741 (1943); Murphy: *Ibid.*, **21**, 863 (1943); *Chem. Met. Eng.*, **50**, 140 (1943).

CHEMICAL STRUCTURES OF DIFFERENT VARIETIES OF SYNTHETIC RUBBERS (FISHER)[24]

(Courtesy of United States Industrial Chemicals, Inc.; reprinted by permission from *Ind. Eng. Chem.*)

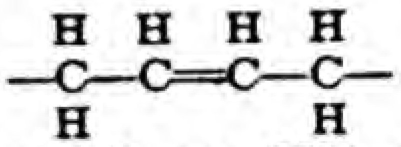
Monomer | Unit of Polymer

SIMPLE POLYMERS

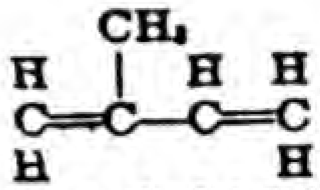

$CH_2{=}CH{-}CH{=}CH_2$

1,3-Butadiene

→

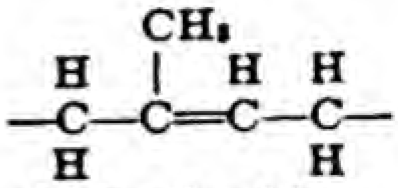

$-CH_2-CH{=}CH-CH_2-$

The numbered Bunas, SKA, SKB, and Ker

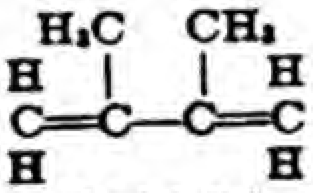

$CH_2{=}C(CH_3){-}CH{=}CH_2$

Isoprene (2-methyl-1,3-butadiene)

→

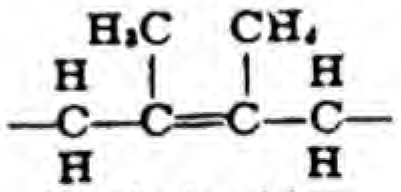

$-CH_2-C(CH_3){=}CH-CH_2-$

Natural rubber

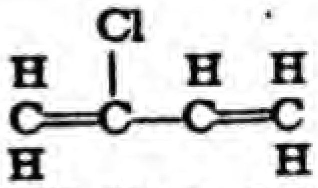

$CH_2{=}C(CH_3){-}C(CH_3){=}CH_2$

2,3-Dimethyl-1,3-butadiene

→

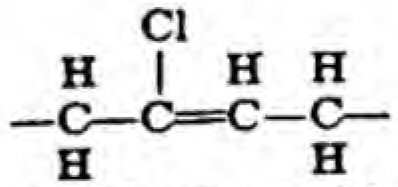

$-CH_2-C(CH_3){=}C(CH_3)-CH_2-$

Methyl rubber

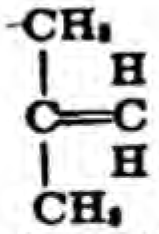

$CH_2{=}CCl{-}CH{=}CH_2$

Chloroprene (2-chloro-1,3-butadiene)

→

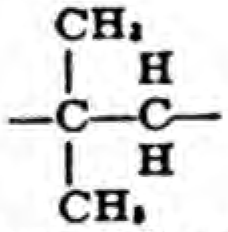

$-CH_2-CCl{=}CH-CH_2-$

Neoprene, Sovprene, Mustone

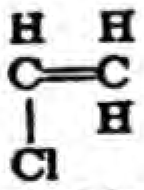

$(CH_3)_2C{=}CH_2$

Isobutylene (2-methylpropene)

→

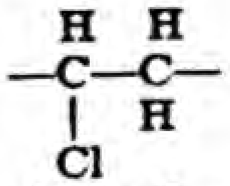

$-C(CH_3)_2-CH_2-$

Vistanex, Oppanol


$CHCl{=}CH_2$

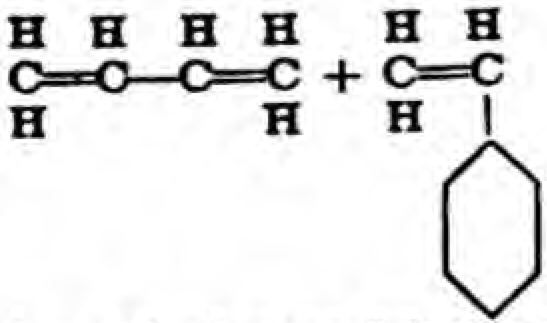
Vinyl chloride

→


$-CHCl-CH_2-$

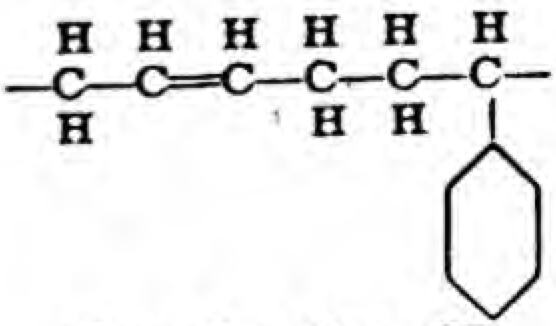
Plasticized polyvinyl chloride materials—Koroseal, Korogel, Flamenol

COPOLYMERS

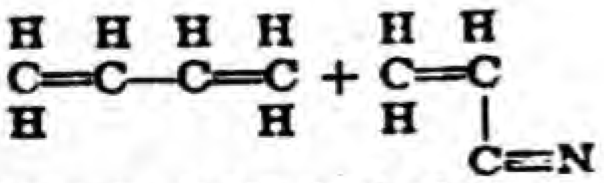


Butadiene + styrene (vinylbenzene)

→

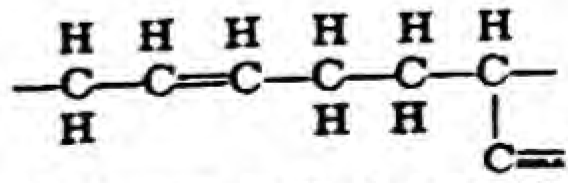


Buna S or Buna SS


$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH{-}C{\equiv}N$

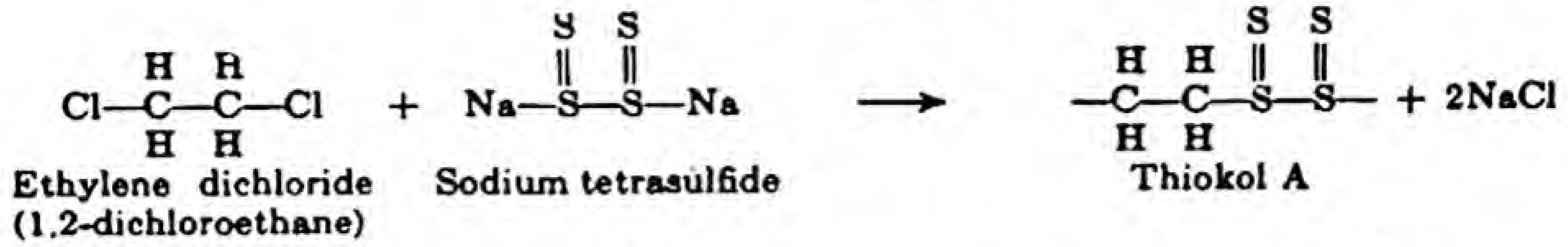
Butadiene + acrylonitrile (vinyl cyanide)

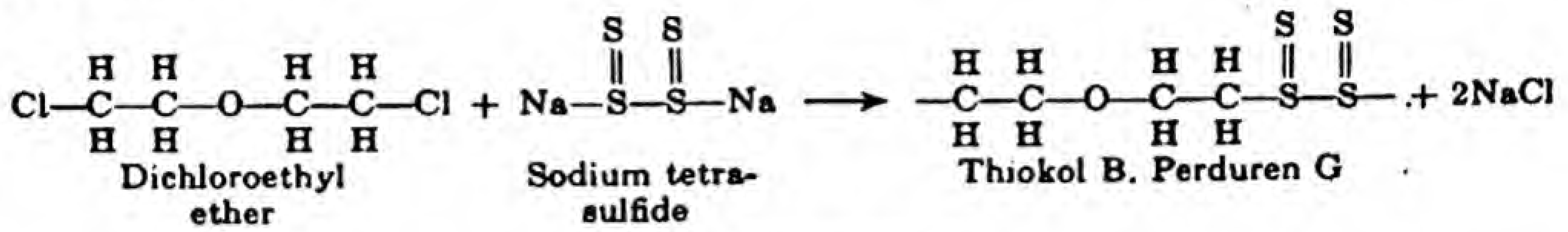
→


$-CH_2-CH{=}CH-CH_2-CH_2-CH(C{\equiv}N)-$

Perbunan or Perbunan Extra

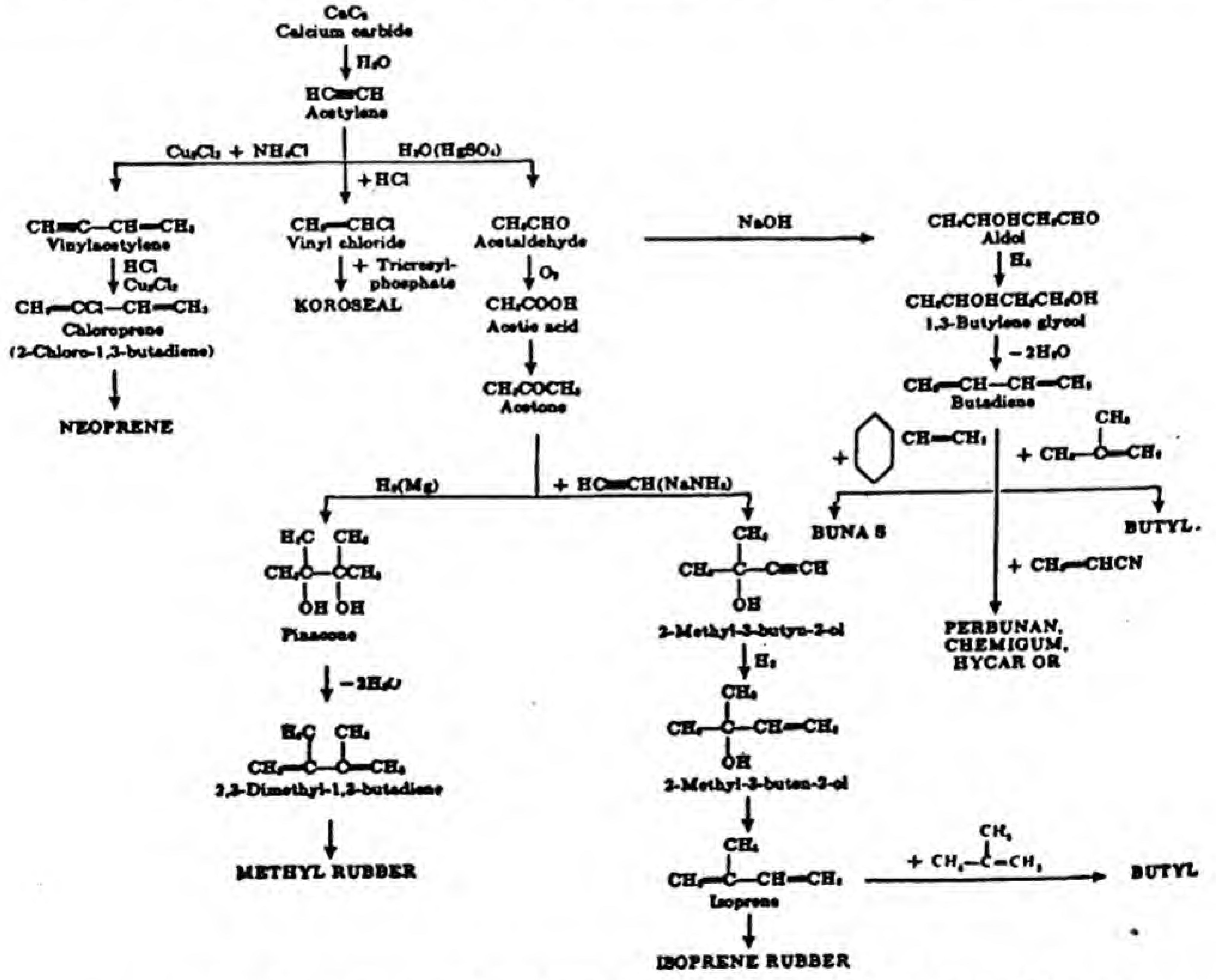
ELASTOTHIOMERS


Ethylene dichloride
(1,2-dichloroethane)
Sodium tetrasulfide
Thiokol A
+ 2NaCl


Dichloroethyl ether
Sodium tetrasulfide
Thiokol B. Perduren G
+ 2NaCl

OTHER COPOLYMERS

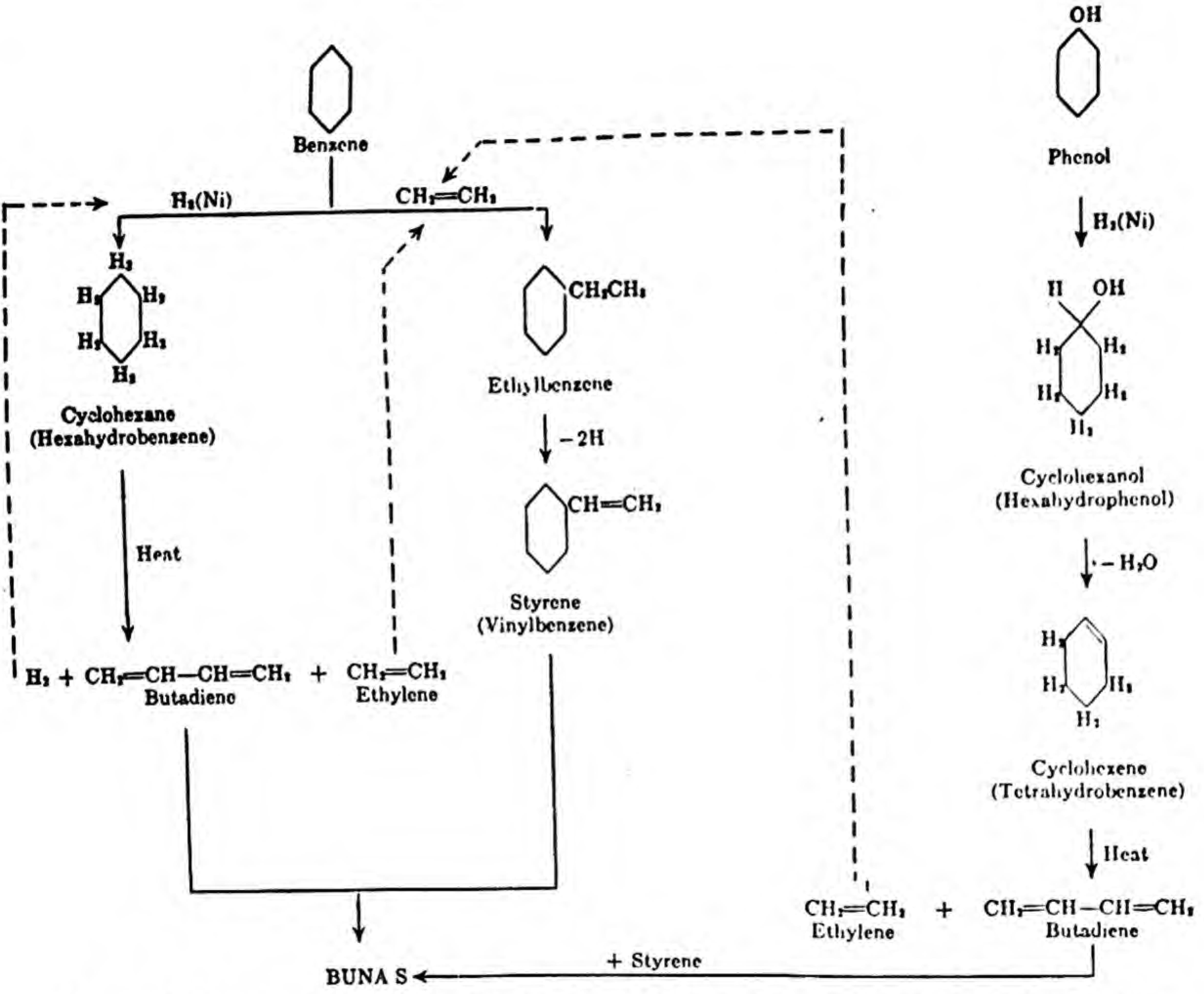
Butyl rubber is a copolymer of isobutylene with a small amount of butadiene or isoprene. Chemigum and Hycar OR are copolymers of butadiene and other substances, the names of which have not been made public, probably acrylonitrile.


CaC2 Calcium carbide
H2O
HC≡CH Acetylene
Cu2Cl2 + NH4Cl
+HCl
H2O(HgSO4)
CH≡C—CH═CH2 Vinylacetylene
HCl Cu2Cl2
CH2═CCl—CH═CH2 Chloroprene (2-Chloro-1,3-butadiene)
NEOPRENE
CH2═CHCl Vinyl chloride
+ Tricresyl-phosphate
KOROSEAL
CH3CHO Acetaldehyde
O2
CH3COOH Acetic acid
CH3COCH3 Acetone
NaOH
CH3CHOHCH2CHO Aldol
H2
CH3CHOHCH2CH2OH 1,3-Butylene glycol
−2H2O
CH2═CH—CH═CH2 Butadiene
CH═CH2
CH3
+ CH2═C—CH3
BUNA S
BUTYL.
+ CH2═CHCN
PERBUNAN, CHEMIGUM, HYCAR OR
H2(Mg)
+ HC≡CH(NaNH2)
Pinacone
−2H2O
2,3-Dimethyl-1,3-butadiene
METHYL RUBBER
2-Methyl-3-butyn-2-ol
H2
2-Methyl-3-buten-2-ol
Isoprene
+ CH3—C═CH2
BUTYL
ISOPRENE RUBBER

FLOW SHEET OF SYNTHETIC RUBBERS PREPARED WITH CALCIUM CARBIDE AS THE STARTING MATERIAL

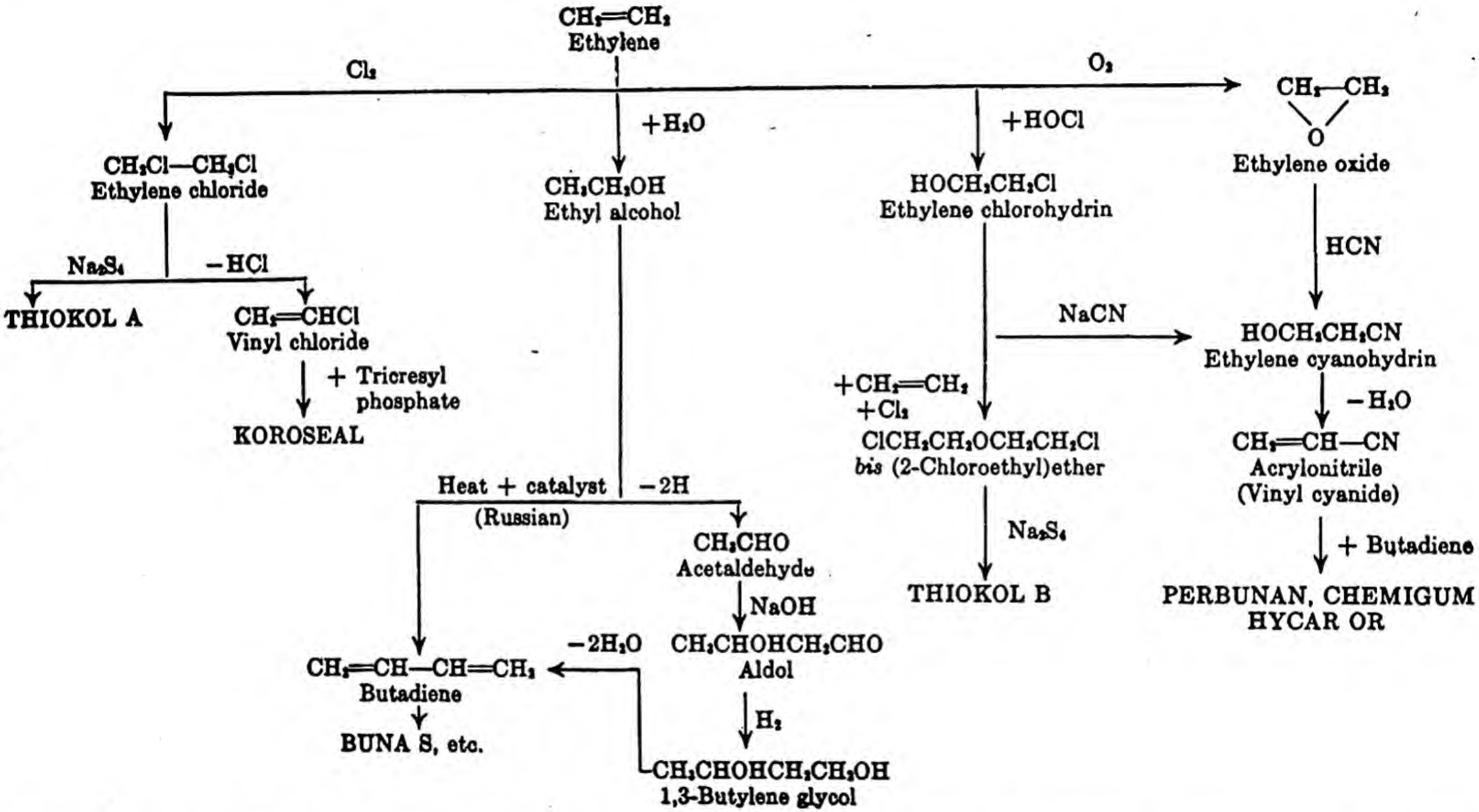
FLOW SHEET OF SYNTHETIC RUBBERS PREPARED WITH CALCIUM CARBIDE AS THE STARTING MATERIAL (FISHER)[24]

(Courtesy of United States Industrial Chemicals, Inc.; reprinted by permission from *Ind. Eng. Chem.*)


Benzene
$H_2(Ni)$
$CH_2{=}CH_2$
Cyclohexane (Hexahydrobenzene)
Heat
$H_2 + CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH_2$
Butadiene
Ethylene
CH_2CH_3
Ethylbenzene
−2H
$CH{=}CH_2$
Styrene (Vinylbenzene)
BUNA S
+ Styrene
OH
Phenol
$H_2(Ni)$
H OH
Cyclohexanol (Hexahydrophenol)
$-H_2O$
Cyclohexene (Tetrahydrobenzene)
Heat
$CH_2{=}CH_2 + CH_2{=}CH{-}CH{=}CH_2$
Ethylene
Butadiene

Flow Sheet of Synthetic Rubbers Prepared with Benzene and Phenol as the Starting Materials (Fisher)[24]

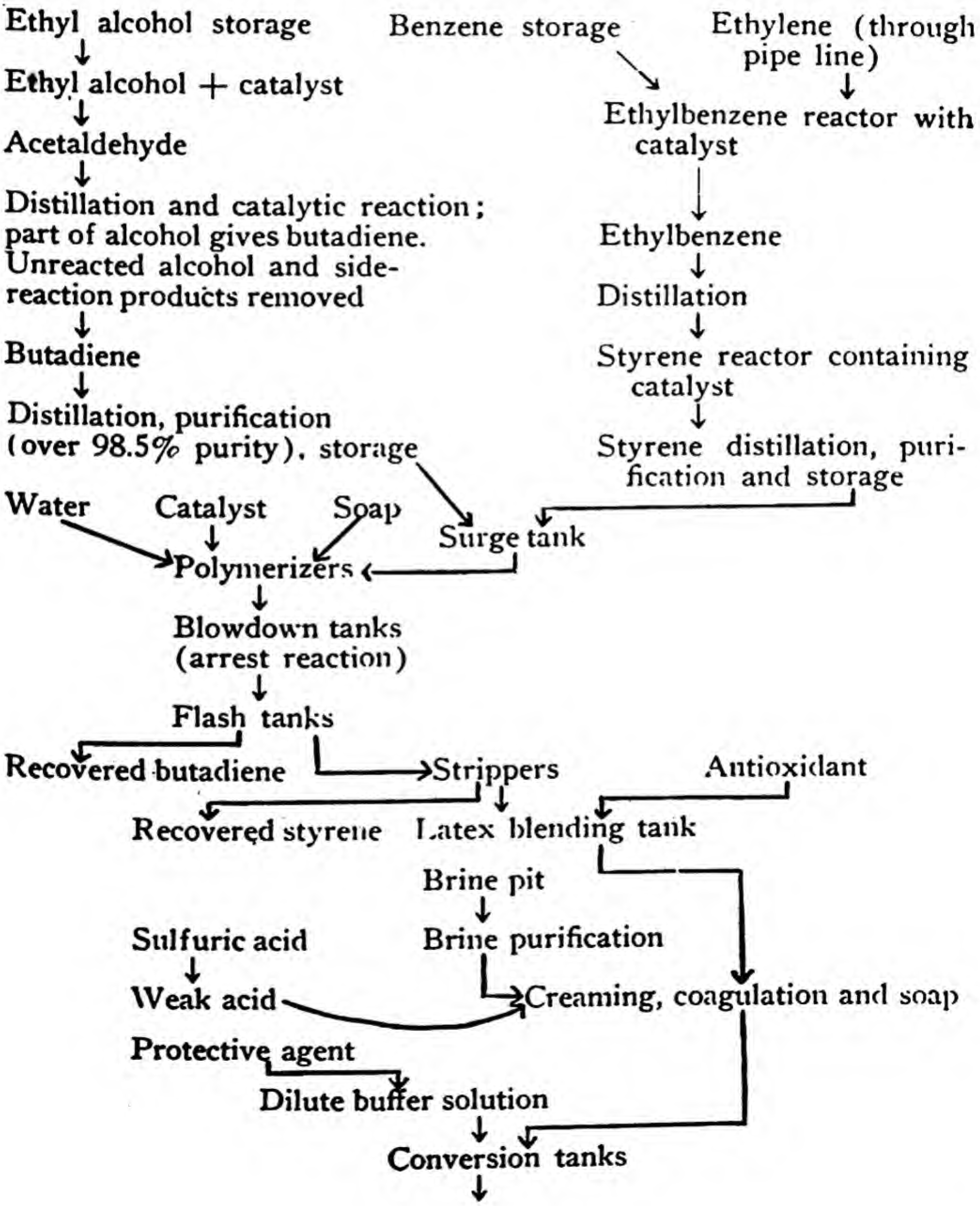
(Courtesy of Industrial and Engineering Chemistry and United States Industrial Chemicals, Inc.)


CH₂=CH₂
Ethylene
Cl₂
O₂
+H₂O
+HOCl
CH₂Cl—CH₂Cl
Ethylene chloride
CH₃CH₂OH
Ethyl alcohol
HOCH₂CH₂Cl
Ethylene chlorohydrin
CH₂—CH₂ O
Ethylene oxide
HCN
Na₂S₄
−HCl
THIOKOL A
CH₂=CHCl
Vinyl chloride
+ Tricresyl phosphate
KOROSEAL
NaCN
HOCH₂CH₂CN
Ethylene cyanohydrin
−H₂O
+CH₂=CH₂
+Cl₂
ClCH₂CH₂OCH₂CH₂Cl
bis (2-Chloroethyl)ether
CH₂=CH—CN
Acrylonitrile
(Vinyl cyanide)
Heat + catalyst
(Russian)
−2H
CH₃CHO
Acetaldehyde
Na₂S₄
THIOKOL B
+ Butadiene
PERBUNAN, CHEMIGUM
HYCAR OR
NaOH
−2H₂O
CH₃CHOHCH₂CHO
Aldol
CH₂=CH—CH=CH₂
Butadiene
BUNA S, etc.
H₂
CH₃CHOHCH₂CH₂OH
1,3-Butylene glycol

Flow Sheet of Synthetic Rubbers Prepared with Ethylene as the Starting Material (Fisher)[24]

(Courtesy of United States Industrial Chemicals, Inc.; reprinted by permission from *Ind. Eng. Chem.*)

A Buna-S rubber is produced by the Defense Plant Corporation at Institute, W. Va. This plant is operated by the Carbide and Carbon Chemicals Corporation and United States Rubber Co. Its capacity is 90,000 tons per year (*Chem. Met. Eng.*, 50, 140, 1943). The flow sheet for this process is as follows:


Ethyl alcohol storage
Ethyl alcohol + catalyst
Acetaldehyde
Distillation and catalytic reaction; part of alcohol gives butadiene. Unreacted alcohol and side-reaction products removed
Butadiene
Distillation, purification (over 98.5% purity), storage
Benzene storage
Ethylene (through pipe line)
Ethylbenzene reactor with catalyst
Ethylbenzene
Distillation
Styrene reactor containing catalyst
Styrene distillation, purification and storage
Water
Catalyst
Soap
Surge tank
Polymerizers
Blowdown tanks (arrest reaction)
Flash tanks
Recovered butadiene
Strippers
Antioxidant
Recovered styrene
Latex blending tank
Brine pit
Brine purification
Sulfuric acid
Weak acid
Creaming, coagulation and soap
Protective agent
Dilute buffer solution
Conversion tanks

Filtering on rotary filter
↓
Washing rubber with fresh water
↓
Disintegrator
↓
Three-pass tunnel dryer
↓
Baler (75 lb loaf)

Note: The emulsion is made from one part of styrene and three parts of butadiene in seven parts of soap solution, a glass lined vessel being used. After removal of unreacted butadiene and styrene, the latex is pumped into a large blending tank where several batches can be mixed so as to obtain a uniform product. Brine is added to the latex in a creaming tank, and the latex is passed into a soap conversion tank where acid is added, and the soap in the reactor is changed to fatty acid. The dilute chemical solution is separated on a rotary filter and the crumbs of rubber are washed with fresh water, etc.

9. Catalytic hydrogenation of vegetable and animal oils and fats

The natural vegetable and animal oils and fats are liquids of low melting point, which is due to a high content of unsaturated fatty acids in the glycerol esters. Furthermore, in their crude state, they have an objectionable odor. By saturating the fatty acids with hydrogen, partly or wholly, more or less solid and deodorized fats are obtained.

By exhaustive hydrogenation of oils, the saturation is practically complete, the oils being transformed into hard and brittle substances almost non-greasy to the feel. The characteristic reaction is one of addition of hydrogen in contact with a catalyst:

$$\underset{\text{oleic acid}}{CH_3\cdot[CH_2]_7\cdot CH{=}CH\cdot[CH_2]_7\cdot COOH} + H_2 \rightarrow$$

$$\underset{\text{stearic acid}}{CH_3\cdot[CH_2]_{16}\cdot COOH}$$

$$\underset{\text{triolein glyceride}}{C_3H_5[OOC\cdot C_{17}H_{33}]_3} + 3H_2 \rightarrow \underset{\text{tristearin glyceride}}{C_3H_5[OO\cdot C_{17}H_{35}]_3}$$

The composition of some oils used in fat hardening is as follows:[1]

---

[1] Richardson, Knuth, and Milligan: *Ind. Eng. Chem.*, 17, 80 (1925).

Oil	Saturated glycerides, %	Olein, %	Linolein, %
Cottonseed	22.6	26.9	50.5
Peanut	40.0	20.5	39.5
Corn	13.0	46.0	41.0
Olive	12.5	80.1	7.5
Leaf lard	37.0	52.4	10.6

The melting points of some fully saturated oils are given in the following table:[2]

Oil	M.p. of the completely hydrogenated oil	Oil	M.p. of the completely hydrogenated oil
Castor	80	Olive	70
Almond	72	Linseed	68

The earliest attempts to solidify oils were by chemical means, such as heating the oil with zinc chloride or phosphorus and iodine, fusing with caustic potash, etc. Sabatier[3] and his collaborators carried out hydrogenation of volatile organic compounds (after 1897) and showed that oleic acid vapors, in the presence of nickel, were transformed into stearic acid. Normann[4] patented a process, in 1902, for catalytic hydrogenation of unsaturated fats in the liquid state, and it is on this principle that the present hydrogenation industries are working.

The technical process, for hydrogenation of edible products of oils and fats, consists of submitting the refined oil (in which a catalyst and filter aid are suspended), to temperatures from 120 to 210°C or higher, although the usual hydrogenation temperatures are between 160 and 180°C or lower. Hydrogen is blown through the oil under a pressure of some few pounds to 50 pounds or more. The hydrogen and oil are mixed by agitation and(or) circulation. The following flow sheet by Wurster[5] illustrates this type of hydrogenation:

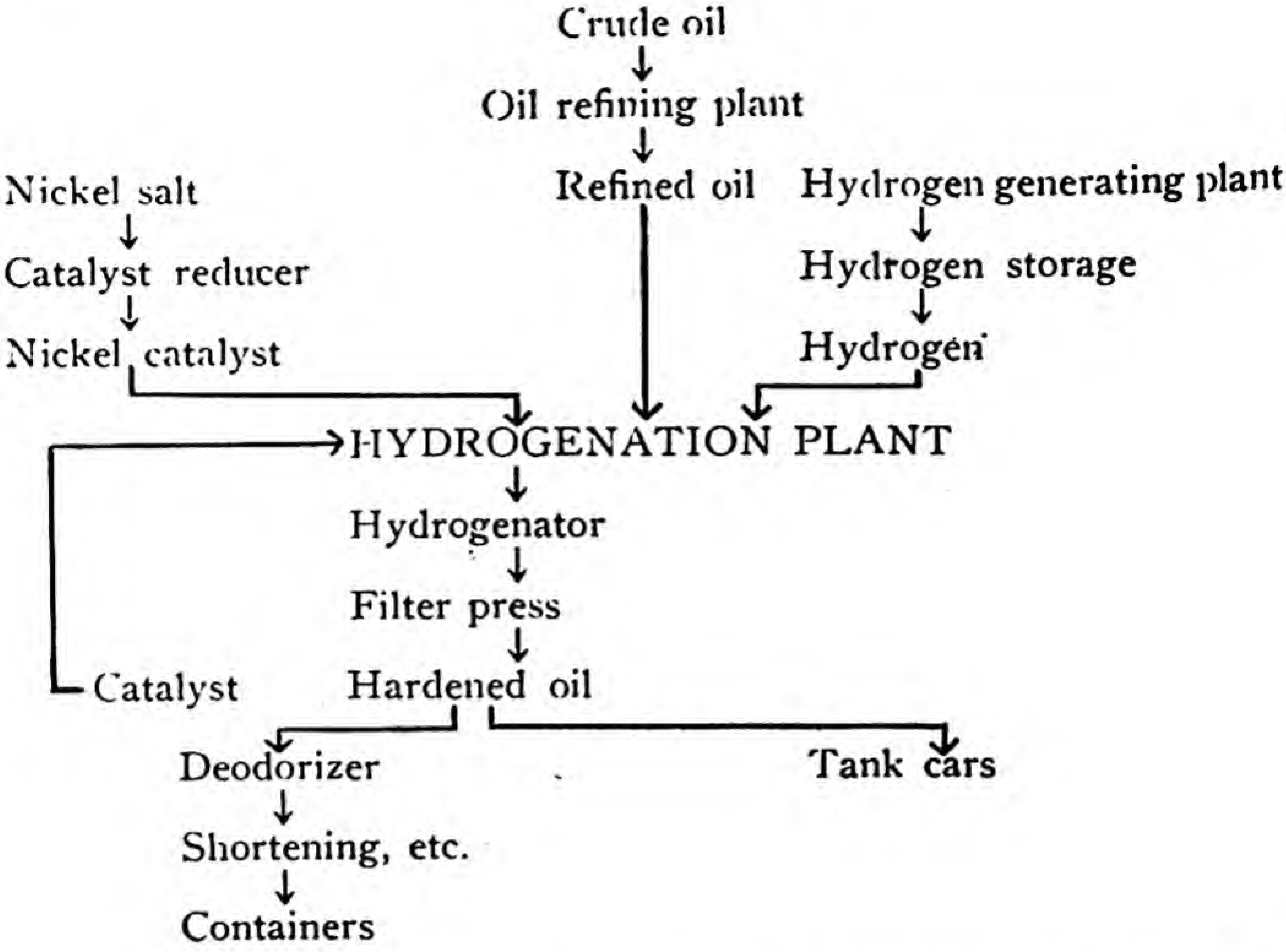
---

[2] Jamieson, G. S.: *Vegetable Fats and Oils*, New York, Reinhold Publishing Corp., 1932.

[3] Sabatier, P.: *La Catalyse en Chimie Organique*, Paris, Librairie Polytechnique, 1920; Sabatier and Reid: *Catalysis in Organic Chemistry*, New York, D. Van Nostrand Co., 1923.

[4] Normann: British Patent 1515 (1903); German Patent 141,029 (1902).

[5] Wurster: *Ind. Eng. Chem.*, 32, 1193 (1940).


Crude oil
Oil refining plant
Nickel salt
Refined oil
Hydrogen generating plant
Catalyst reducer
Hydrogen storage
Nickel catalyst
Hydrogen
HYDROGENATION PLANT
Hydrogenator
Filter press
Catalyst
Hardened oil
Deodorizer
Tank cars
Shortening, etc.
Containers

The layout of a plant of this type is presented in figures 29 and 30.

Different technical procedures are in use for mixing of the oil and the hydrogen during the hydrogenation operation.

Agitation plants. In these plants, the hydrogen enters at the bottom of the converter and is mixed with the oil and catalyst by mechanical agitation. The size of converters, for this process, is from some few tons up to 20 tons. Cylindrical converters are most frequently used, supplied with closed coils for cooling or heating. The hydrogenation process is strongly exothermic, and in order to keep the hydrogenation temperature constant, cooling during hydrogenation is required, especially at low hydrogenation temperatures. This type of plant is best suited for processing with a high content of catalyst and filter aid, and for use with impure hydrogen gas, as the accumulation of impurities is readily prevented. The pressure used is mostly low, i.e., from 15 to 50 pounds per square inch.

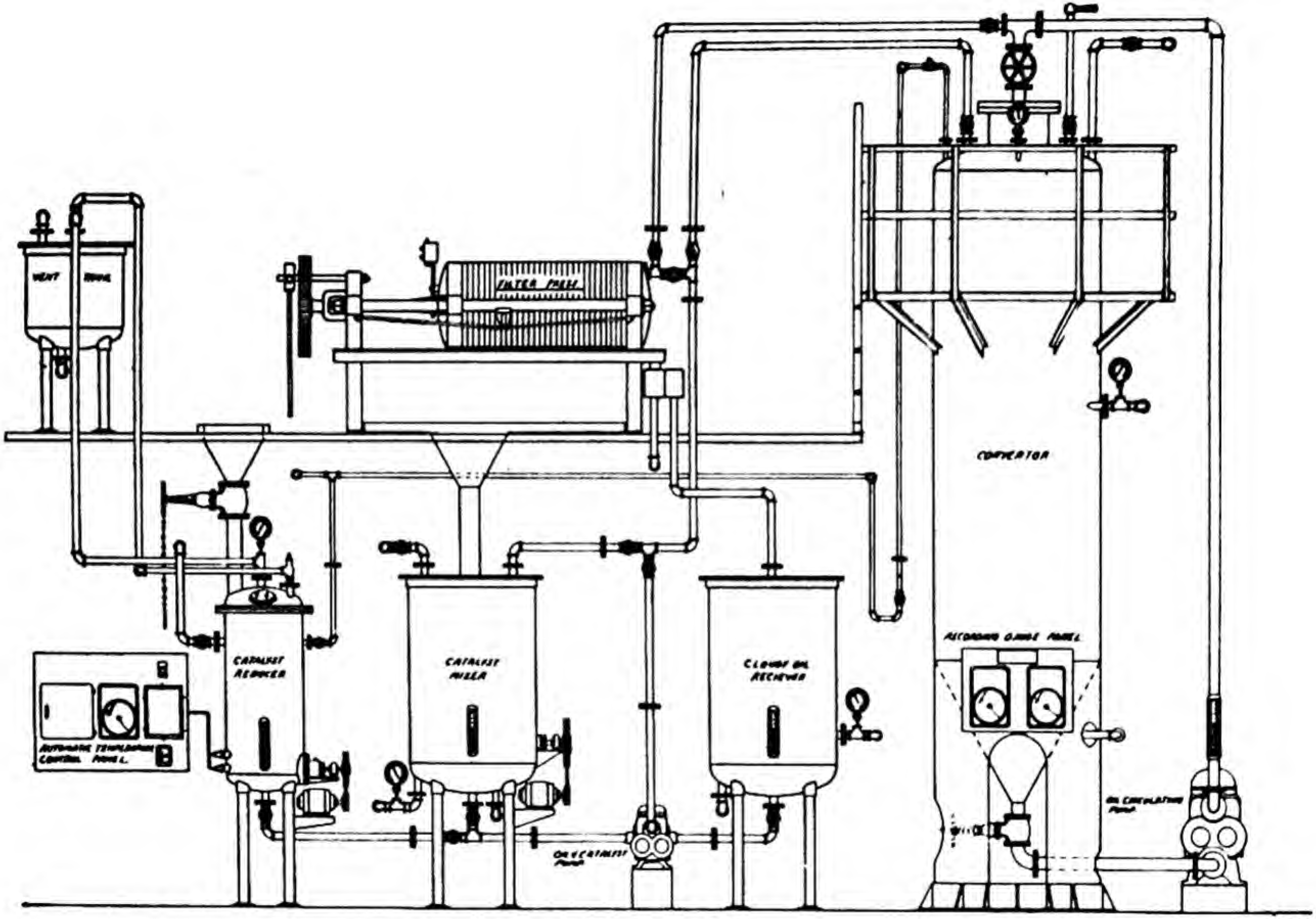

VENT TANK
FILTER PRESS
AUTOMATIC TEMPERATURE CONTROL PANEL
CATALYST REDUCER
CATALYST MIXER
OIL & CATALYST PUMP
CLOUDY OIL RECEIVER
CONVERTOR
RECORDING GAUGE PANEL
OIL CIRCULATING PUMP

FIGURE 29

HYDROGENATION PLANT USING NICKEL FORMATE CATALYST

(Courtesy of Wurster & Sanger, Inc., Chicago, Ill.)

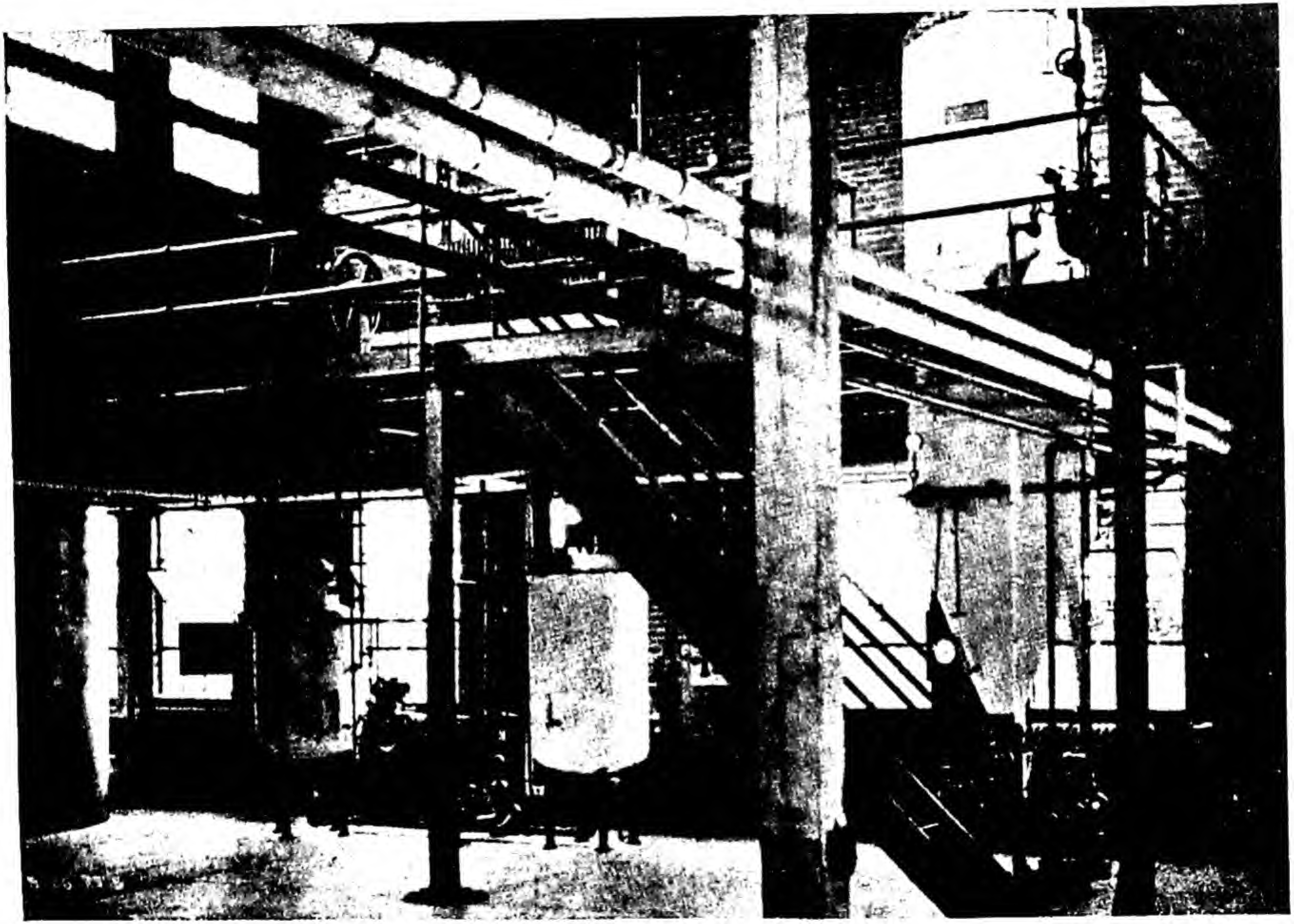


FIGURE 30

HYDROGENATION PLANT SHOWING REDUCER, MIXING TANK, FILTER PRESS, AND CONVERTER

(Courtesy of Wurster & Sanger, Inc., Chicago, Ill.)

Recycling plants. In this type of plant, the oil and catalyst mixture is circulated through an atmosphere of hydrogen. In a process by Testrup,[6] the oil and catalyst are passed through tanks with decreasing pressure by means of spray nozzles. In the process by Maxted and Ridsdale,[7] the mixture of the oil with the suspended catalyst and the hydrogen is afforded by means of a mixing column, in which the oil and gas are brought into intimate contact by the action of fixed propeller-like baffle plates, which are shaped and placed in such a way that the moving liquid-gas mixture is rotated, alternately, clockwise and anti-clockwise. The oil and catalyst mix is recirculated by a pump, and the degree of mixing of hydrogen and oil is regulated by the rate at which the oil pump and compressor are operated. The operating pressure of hydrogen, for this process, is about fifty to sixty pounds. The hydrogenation is claimed to proceed rapidly at comparatively low temperature, e.g., 130°C initial temperature, making it a very good process for the manufacture of edible products.

The above mentioned processes are batch processes with the catalyst suspended in the oil. In plant practice, a combination of agitation and recycling is used to advantage.[5]

Continuous hydrogenation plants.[8] The continuous process involves the passing of the oil-hydrogen mixture over a catalyst surface, which may be in the form of a wire screen, turnings, or perforated discs. In all cases, the catalyst is maintained as a separate body, so that the catalyst is not mixed with the oil to be hydrogenated, thus obviating the necessity of separating the catalyst from the hydrogenated product. In the process of the Technical Research Works Limited,[8] the catalyst consists of specially designed and constructed pure nickel elements consisting of perforated discs assembled in blocks or bundles. The catalyst blocks are made to fit exactly into the reactor in which the hydrogenation takes place. Activation is carried out by anodic oxidation in a solution of sodium carbonate. The oxygen, liberated at the anode, causes the metallic nickel surface to be converted into nickel oxide, which is reduced in a current of hydrogen for about eight hours. The metallic nickel surface may also be oxidized by steeping the blocks (or whatever form of nickel metal is used) in a sodium hypochlorite solution.

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[6] Testrup: British Patent 7726 (1910).

[7] Maxted and Ridsdale: *J. Soc. Chem. Ind.*, **36**, 1185 (1917); British Patent 109,993 (1913); Maxted: U. S. Patent 1,313,407 (1919).

[8] Bolton: *J. Soc. Chem. Ind.*, **41**, 384 R. (1922); *ibid.*, **46**, 444T (1927); Lush: *J. Soc. Chem. Ind.*, **42**, 219T (1923); *ibid.*, **43**, 53T (1924); *ibid.*, **44**, 129T (1925); *ibid.*, **46**, 454T (1927); Lush and Technical Research Works Limited, British Patents, 203,218 (1922), 221,000 (1923) and 241,278 (1924).

The oil to be hydrogenated is admitted at the top of the converter and trickles down over the catalyst surface, meeting on its way down an upward current of hydrogen. The hydrogenated oil is continuously removed at the bottom of the converter and the hydrogen is collected at the top and reused. This type of process, operating with a closed converter, requires pure hydrogen to prevent the detrimental accumulation of catalyst poisons from the gas. The hydrogen pressure, used in this process, is about 50 to 100 pounds, and the hydrogenation temperature about 180°C.

The oil or fat is refined before hydrogenation, to prevent the foots and other impurities from impairing the activity of the catalyst and the color of the oil. The following substances, in oils and fats, are considered detrimental to the activity of the catalyst: [5, 9, 10]

Soaps
Oxidized fats
Gelatin and decomposition products
Albuminous matter
Proteins
Phosphatides
Organic and inorganic sulfur compounds
Organic and inorganic chlorine compounds
Water
Free fatty acids in high content

In hardening soybean oil with a nickel-copper catalyst, the various metallic soaps influenced the catalyst differently: [11]

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[9] Ellis and Wells: *Ind. Eng. Chem.*, **8**, 886 (1916).

[10] Deem and Kaveckis: *Ibid.*, **33**, 1373 (1941).

[11] Ueno, Miayake, and Anzai: *Chem. Abstracts*, **35**, 3113 (1941).

1. *Negative catalysts:* * Soaps of *K*, *Na*, Mn, Zn, Cd, Fe, Pb, (Co), (Ca), (Mg), (Ba), (Co)
2. *Indifferent:* Soap of Al
3. Positive catalysts: Soaps of *Ni*, Ag, (Cu)

For the economy of the hardening, it should be noted that the more the oil is refined the less catalyst is required. This is true both in the concentration of the catalyst used and the number of times a catalyst can be used before it has to be reactivated.

The hydrogenation of the unsaturated glycerides or acids is progressive, the most unsaturated glycerides being converted first. The order of saturation is substantially as follows:

$$\begin{aligned} &\text{Linolenic} + H_2 \rightarrow \text{Linoleic} \\ &\text{Linoleic} + H_2 \rightarrow \text{Oleic} \\ &\text{Oleic} + H_2 \rightarrow \text{Stearic (saturated)} \end{aligned}$$

According to Hilditch and Hall,[12] all three stages proceed to some degree concurrently, but only one ethenoid group, in a complex triglyceride molecule, appears to be saturated with hydrogen at any one contact with the catalyst. This progressive order of saturation with hydrogen is termed selectivity. The lowering of the linoleic acid content is very important, to insure the keeping quality of partially hydrogenated products. Lower pressure and rapid reaction seem to favor selectivity.[13] If high hydrogen pressures are used, completely saturated compounds are formed in appreciable quantities from the start.[14]

The selective progress of the hydrogenation of oils and fats was studied first by American workers [15, 16] and later by Hilditch and his associates.[12, 18] In studying various oils, Richardson, Knuth, and Milligan [16] found that by hydrogenation of cottonseed, peanut and soybean oils with a nickel catalyst, there was a preferential conversion of linoleic acid to oleic acid and its isomers. The selective hydrogenation of linoleic acid appeared to be more marked with use of increasing amounts of catalyst and with increasing temperature up to an optimum in the neighborhood of 200°C.

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* Strong action is indicated by italicizing, and mild action by parentheses.

[12] Hilditch, T. P., and C. C. Hall: *Catalytic Processes in Applied Chemistry*, London, Chapman and Hall Limited, 1937.

[13] Lazier, W. A.: *Progress in the Catalytic Hydrogenation of Fats and Oils*, Twelfth Report of the Committee on Catalysis, National Research Council, New York, John Wiley and Sons, Inc., 1940.

[14] Waterman and Vlodrop: *Chimie & industrie*, Special No., 902, (April, 1934).

[15] Moore, Richter, and Van Arsdel: *Ind. Eng. Chem.*, **9**, 451 (1917).

[16] Richardson, Knuth, and Milligan: *Ibid.*, **16**, 519 (1924).

Selective hydrogenation of refined cottonseed oil with 0.2% nickel at 175°C (Richardson, Knuth, and Milligan).[16]

		Composition of mixed acids, %			
Iodine value	Solid acids, %	Saturated acids	Oleic	Isooleic	Linoleic
109.8 (original)	23.1	22.7	27.1	0.4	49.8
73.7	42.3	24.8	47.5	17.5	10.2
71.7	47.6	25.4	43.9	22.2	8.5
69.7	44.2	25.5	49.4	18.7	6.4
65.2	52.2	28.4	43.7	23.8	4.1
52.0	63.5	38.7	36.5	24.8	0
49.4	62.5	42.1	37.5	20.4	0
45.4	65.8	45.9	34.2	19.9	0

In a study, by the same workers, on marine oil, whale, and menhaden oils, it was found that the selectivity was not so marked. Above an iodine value of 84, the C_{20} and C_{22} acids, with two double bonds, are converted into acids with one double bond. At an iodine value of 84, an abrupt change occurs, and below this value, hydrogenation results both in formation of saturated acids and in the conversion of the C_{20} and C_{22} acids containing two double bonds into corresponding acids containing one double bond.

In hydrogenating cottonseed oil for one and a half hours at 180°C and 25 atmospheres pressure,[17] it was found that the content of saturated fatty acids did not increase greatly until the content of oleic acid had reached its maximum. The content of isooleic acid showed the highest value at about half an hour from the start of the reaction, and at this time, linoleic acid disappeared. This observation is in agreement with results obtained by Hilditch and his associates,[18] and as they very strikingly put it: "During hydrogenation, all the highly unsaturated fats pass through a stage corresponding to that of olive oil before they proceed to complete saturation."[12]

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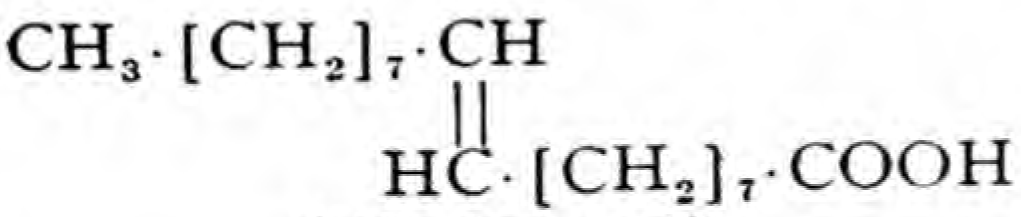
[17] Ueno and Tokunaga: *J. Soc. Chem. Ind. Japan,* **43,** Suppl. binding 292–4 (1940); *Chem. Abstracts,* **35,** 1255 (1941).

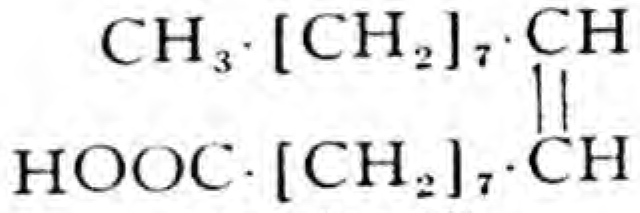
[18] Hilditch et al.: *J. Chem. Soc.,* 805 (1932); *J. Soc. Chem. Ind.,* **42,** 15T (1923); *ibid.,* **51,** 198T, 202T (1932); *ibid.,* **54,** 77T, 331T (1935); *ibid.,* **55,** 95T (1936); *Biochem. J.,* **29,** 90 (1935).

In partially hydrogenated oils and fats, some stearic glyceride is formed, together with considerable amounts of isooleic and other oleic glycerides derived from the hydrogenation of linoleic glycerides. Isooleic acid is a mixture of elaidic acid (solid), which is a transisomeride of the ordinary 9:10 oleic acid, and another solid acid, probably the 11:12 oleic acid:[19, 21]



$$\begin{array}{l}\mathrm{CH_3\cdot[CH_2]_7\cdot CH}\\ \qquad\qquad\quad \| \\ \qquad\qquad\quad \mathrm{HC\cdot[CH_2]_7\cdot COOH}\end{array}$$

elaidic (trans-acid)



$$\begin{array}{r}\mathrm{CH_3\cdot[CH_2]_7\cdot CH}\\ \| \\ \mathrm{HOOC\cdot[CH_2]_7\cdot CH}\end{array}$$

oleic (cis-acid)

The lower the hydrogenation temperature, the less isooleic acid is formed. Evidence from infra-red and Raman spectroscopic examinations of the unsaturated C_{18} fatty acids has led to the conclusion that the naturally occurring acids, such as oleic, linoleic, and linolenic, contain only cis-double bonds, whereas the artificial elaidic and linelaidic acids contain only the trans linkages.[20]

In making shortening from cottonseed oil, in the United States, the hydrogenation is carried on to the following values (Jamieson):[18]

		Percentage of fatty acids		
M.P. °C	**Iodine value**	**Saturated**	**Oleic**	**Linoleic**
34–53	60–75	27–33	7–18	5–12

Due to the selectivity of the hydrogenation reaction, the composition of a hardened oil, mixed with the original oil or a less hardened oil to provide definite saturation, is not the same as that of an oil hardened to the same degree in bulk (Hilditch and Hall).[12]

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[19] Jamieson, G. S.: *Vegetable Fats and Oils*, Am. Chem. Soc. Monograph, Reinhold Publishing Corporation, 1932.

[20] McCutcheon, Crawford, and Welsh: *Oil & Soap*, **18**, 9 (1941).

[21] Hilditch: *Proc. Roy. Soc. (London)*, **A122**, 552 (1929).

The isooleins are objectionable because the soaps of the solid oleic acids are less soluble and possess less lathering power than the soaps of ordinary oleic acid. The solid isooleins tend to affect the consistency and appearance of the edible fats in which they are present.[21]

In the continuous hydrogenation process, the layer of oil nearest the catalyst tends to become more completely hydrogenated than the rest, the result being that for the same degree of saturation, an oil, hydrogenated by the continuous process, will contain more completely saturated glycerides, less isooleic derivatives, and less selective hydrogenation of linoleic glycerides to oleic, than the product obtained by agitating the oil, catalyst and hydrogen together.[22]

The degree of saturation, during the hydrogenation process, is controlled by various tests, the quickest one of which is determination of the refractive index which takes only a few minutes. For quick plant control, curves are drawn for the oils to be hardened which show the iodine number, melting point, and/or titer corresponding to the refractive index.[5]

The hydrogen, used for hydrogenation, must be as pure as possible. Inert gases, such as nitrogen, are not harmful. Carbon monoxide is a serious catalyst poison for this hydrogenation reaction below 200°C and, if not removed from the gas, it is also apt to cause shorter life of some types of nickel catalysts. Sulfur dioxide, hydrogen sulfide, carbon disulfide and organic sulfur compounds are also strong catalyst poisons. Typical compositions of hydrogen used for hydrogenation on the North American continent are as follows:[5]

	Composition %*				
Process	Hydrogen	Oxygen	CO	CO_2	N_2
Electrolysis	99.75	0.05	...	...	0.20
Steam-iron	99.1	...	0.1	0.2	0.6

One ton of oil absorbs theoretically thirty cubic feet of hydrogen gas for each point of reduction in iodine value. With high quality electrolytic hydrogen, the actual hydrogenation consumption is usually from 105 to 110 per cent of the theoretical; and with less pure hydrogen, e.g., that from the steam-iron process, the hydrogen consumption may reach up to 120 per cent of the theoretical.

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[22] Hilditch and Rhead: *J. Soc. Chem. Ind.*, 51, 198T (1932).

The velocity of the hydrogenation, V, is determined by the activity of the catalyst, the temperature, and the pressure of the hydrogen gas. A certain catalyst and temperature given, the velocity of hydrogenation is given by:[23, 24]

$$V = K \cdot C_1 \cdot C_2$$

where K is a reaction constant, C_1 the active mass of the oil, and C_2 the active mass of the hydrogen. Consequently, in plant design $C_1 \cdot C_2$ should be as large as possible, i.e., the hydrogen pressure as high as permissible, and the pumps correspondingly strong. It also follows that high activity of the catalyst is of great advantage.

The rate of reaction is determined by:

$$\frac{dx}{dt} = K\,(a - x)\text{, consequently, } K = \frac{1}{t} \cdot \ln \frac{a}{a - x}.$$

Where "a" is the total saturation of the oil with respect to hydrogen, and "x" the degree of saturation at the time t. According to this equation, the hydrogenation reaction proceeds as a monomolecular process. The hydrogenation reaction is exotherm:[24]

$$C_nH_{2n} - mO_2 + mH \rightarrow C_nH_{2n}O_2 + q$$

where q is the number of calories evolved per mole by full saturation of the fatty acid. Some examples of the numerical values of q, for different substances, are the following:

	q, in calories per mole		q, in calories per mole
Oleic acid	25,000	Ground nut oil	25,500
Castor oil	24,500	Soybean oil	26,100

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[23] Martin, G.: *Industrial and Manufacturing Chemistry, Part I. Organic*, London, Crosby, Lockwood and Son, 1920.

[24] Holmboe: *Ber.*, **71**, 532 (1938).

If, in the case of oleic acid, 0.1 per cent of metallic nickel has been used as catalyst, one mole oleic acid is hydrogenated by 0.28 grams of nickel, i.e., about 89,000 calories are evolved per one gram of nickel. However, only a small fraction of the nickel atoms is active, and if one out of a thousand nickel atoms is reactive, one gram of reactive nickel evolves 89,000,000 calories per hour. For comparison, the heat of combustion of charcoal to carbon dioxide is about 8,100,000 calories per gram. Although these figures are concerned with magnitudes only, it is seen that the local evolution of heat is of very considerable proportions.

Many catalysts for hydrogenation of oils and fats, as discussed above, have been proposed, viz., Ni, Fe, Co, Cu, Mo, W, U, V, Mn, Ta, platinum metals, mixed metal and oxide catalysts, etc. However, the usual catalyst, for hydrogenating vegetable and animal oils and fats (except for high temperature and pressure hydrogenation), is nickel, although, to a minor extent, certain oxides and noble metals are also used.

The importance of catalytic hardening of oils follows from the fact that in 1936, the fat hardening industry in the United States had a total output of about 420,000 tons, and the rest of the world had at least an equal output. In 1936, 467,000 pounds of nickel were used for catalytic purposes in North America, and of this, a little more than 300,000 pounds were used for the hardening of oils.[25]

Form and quantities of nickel used for catalytic purposes in North American countries in 1936 (*Fraser*)

Form of nickel	Weight of contained nickel, lb
Sulfate	291,860
Formate	41,300
Carbonate	10,100
Oxide	850
Nitrate	40
Metallic	123,350
Total	467,500

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[25] Fraser: *Trans. Electrochem. Soc.*, **71**, 1 (1937).

On this, Fraser[25] comments that "it is noteworthy that nickel hydroxide, which was included a few years ago, no longer appears in the list of purchased catalyst raw materials." The probable reason for this is that, in later years, the plants using nickel hydroxide make it themselves, either electrochemically from metallic nickel or from the sulfate or nitrate. Fraser reports that England and France, in 1936, used about 250,000 pounds of nickel for fat hardening. Very substantial quantities of nickel were also used for the same purpose in other countries, particularly in Germany. An appreciable quantity of nickel, for catalytic fat hardening, is derived from regenerated spent nickel catalyst, which is not taken into account in the foregoing table. A large proportion of the nickel sulfate, used for fat hardening, is made as a by-product of copper refining and is, in purity, below the standard for refined nickel. A few years ago, mixed nickel and copper carbonates were sold in substantial quantity. The carbonates were reduced together to a catalyst active at lower temperature than is a pure nickel catalyst. It should be added that, in later years, reduced active nickel catalysts, in hardened oil, were on the market, such catalysts containing 20 to 23 per cent of metallic nickel.

Some interesting work has been carried out with hydrogenation of oils, in the presence of a nickel catalyst, using alcohols as hydrogen donors. Actually, this process is carried out under conditions that the alcohol is dehydrogenated and the oil is hydrogenated by the liberated hydrogen:[26, 27]

$$\mathrm{R{\cdot}CH_2OH} \xrightarrow{\text{Ni catalyst}} \mathrm{R{\cdot}CHO} + \mathrm{H_2}$$

In processing soybean oil, in the presence of Normann's nickel catalyst, using propyl alcohol as a hydrogen donor, the following data were obtained:

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[26] Rush and Dvinyaninova: *J. Applied Chem. (U.S.S.R.)*, **12**, 428 (1939); *Chem. Abstracts*, **33**, 6629 (1939).

[27] Rush and Dvinyaninova: *Ibid.*, **12**, 1060 (1939); *Chem. Abstracts*. **34**, 3116 (1940).

Constituents	Before processing, per cent	After processing, per cent
Oleic acid	20.1	74.5
Linoleic acid	71.2	9.6
Isooleic acid	—	4.8
Saturated acids	8.7	11.1

The yield of aldehyde was 21.7 per cent of the theoretical, 17.3 per cent aldehyde was decomposed, and the balance was not accounted for.

10. Hydrogenation of fatty acids and oils for production of higher alcohols and esters

The reduction of esters by means of sodium and anhydrous alcohol to the corresponding alcohols[1] has been known by now for about four decades:

$$R{\cdot}COOR' + 2H_2 \rightarrow R{\cdot}CH_2OH + R'OH$$

By hydrogenation, at about 200°C, and 150 to 200 atmospheres pressure, the acids and esters, in the triglycerides in oils or in natural fatty acids, are converted into the corresponding alcohols. The ethylenic unsaturated group is not necessarily hydrogenated under these conditions, but may be so at lower temperature and pressure using nickel catalyst. The choice of catalyst to be used in this process depends on what products are desired. When a copper catalyst is used, the corresponding alcohols, free from hydrocarbons, are formed. Above 250°C, using ordinary nickel catalyst, hydrocarbons are formed as the major products, the carboxyl group also being reduced.[2, 4, 6, 7] Using zinc chromite, unsaturated alcohols are produced.[3, 4] Other catalysts are copper chromite, basic copper chromate, zinc-copper chromate, nickel copper zincate, molybdenum, etc.[5]

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[1] Bouveault and Blanc: *Bull. soc. chim.*, **31**, 1210 (1904).

[2] Lazier, W. A.: *Progress in the Catalytic Hydrogenation of Fats and Oils*, Twelfth Report on Catalysis. National Research Council, New York, John Wiley and Sons, Inc., 1940, p. 131.

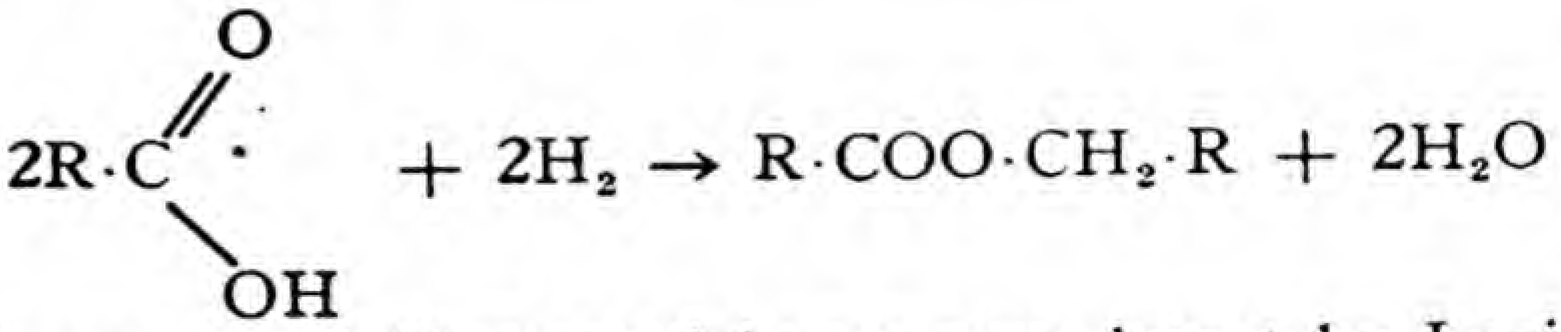
[3] Adkins and Sauer: *J. Am. Chem. Soc.*, **59**, 1 (1937).

[4] Lazier: U. S. Patents 1,839,947 (1932), 1,964,000 (1934), 2,077,421 (1937), 2,094,127 (1937), 2,094,611 (1937), 2,079,414 (1937), and 2,109,844 (1938).

[6] Lazier: U. S. Patent 1,839,974 (1932).

[7] Lazier: U. S. Patent 2,109,844 (1938).

In the above reaction, esterification of part of the alcohol, formed with the unchanged acid, takes place as a secondary reaction, the amount of ester formed depending on the completeness of the hydrogenation. If the acid is only partially reduced, esters are the main products:[5]



$$2R\cdot C\begin{matrix}\nearrow O \\ \searrow OH\end{matrix} + 2H_2 \rightarrow R\cdot COO\cdot CH_2\cdot R + 2H_2O$$

This is very well illustrated in an experiment by Lazier,[6] who hydrogenated pure oleic acid in the temperature range from 350 to 420°C, using a pressure of 2,800 pounds per square inch. It was found that the lower temperatures favor the formation of waxes, which at the higher temperatures are hydrogenated to free alcohols:

	Composition of product, per cent			
Temp., °C	Acid	Ester	Alcohol	Total
350	19	36	39	94
360	8	36	50	94
370	6	34	58	98
390	2	30	68	100
400	2	29	67	98
410	2	26	65	93
420	1	21	60	82

In another patent, Lazier[7] hydrogenates glycerides of aliphatic carboxylic acids, the resulting material being a mixture of alcohols and waxy esters of the alcohols free from hydrocarbons. The catalyst used is a mild-acting alcohol-forming hydrogenation catalyst at a temperature above 200°C and above 13.5 atmospheres.

If nickel is used as catalyst at 250°C, and 100 to 200 atmospheres of hydrogen pressure, the alcohols are converted almost quantitatively into paraffin hydrocarbons and methane:

$$R\cdot CH_2OH + 2H_2 \rightarrow RH + CH_4 + H_2O$$

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[5] Fenske, M. R.: Hydrogenation, Chapter VIII of Groggin's "Unit Processes in Organic Synthesis," New York, McGraw-Hill Book Company, 1938, p. 419.

The technical importance is considerable, as the higher alcohols and esters are valuable as waxes and the individual alcohols may be separated by fractional distillation under reduced pressure. Furthermore, the alkali salts of the hydrogen sulfates of the higher fatty alcohols are widely used as detergents, wetting-out agents, emulsifiers, etc.

Conversion of vegetable fats into hydrocarbons has been tried out by several workers. Mailhe[11] decomposed vegetable oils by heating them in contact with chlorides or oxides of calcium, magnesium, zinc or tin; the yield was 50 to 65 per cent of the original weight of the oil. Dry distillation of magnesium and calcium soaps of vegetable oils resulted in oils which were readily hydrogenated in the presence of nickel. Pressure hydrogenation cracking at or above 430°C, and thermal decomposition in the presence of active charcoal of soybean oil also has been investigated.[12]

GENERAL REFERENCES

Adkins and Connor: *J. Am. Chem. Soc.*, **53**, 1091 (1931); Adkins and Folkers: *Ibid.*, **53**, 1095 (1931); Wojick and Adkins: *Ibid.*, **55**, 1293 (1933).

11. Dehydration of castor oil

The purpose of dehydration of castor oil is to increase the unsaturation of the oil in order to improve its drying properties. This treatment was originally intended for making a substitute for tung oil, but dehydrated castor oil is by now recognized as an independent vehicle and is used more often by itself than with other oils (von Mikusch).[1]

Dehydrated castor oil contains about 85 per cent of the triglycerides or mixed glycerides of 9,12- and 9,11-linoleic acids with a little oleic acid, and a few per cent of hydroxy acids, but no more than in most natural drying oils. Saturated acids are present in traces only, and linolenic acid is absent.

The 9,12-linoleic acid, containing two double bonds in isolated position, is a stereoisomer of the 9,12-linoleic acid in vegetable oils, such as linseed, perilla, and soybean oils, which contain nothing or practically nothing of the 9,11-oleic acid.

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[11] Mailhe: British Patent 218,278 (1925).

[12] Hilditch, T. P., and C. C. Hall: *Catalytic Processes in Applied Chemistry*, London, Chapman and Hall, 1937, p. 295.

[1] von Mikusch: *Ind. Eng. Chem.*, **32**, 1061 (1940)

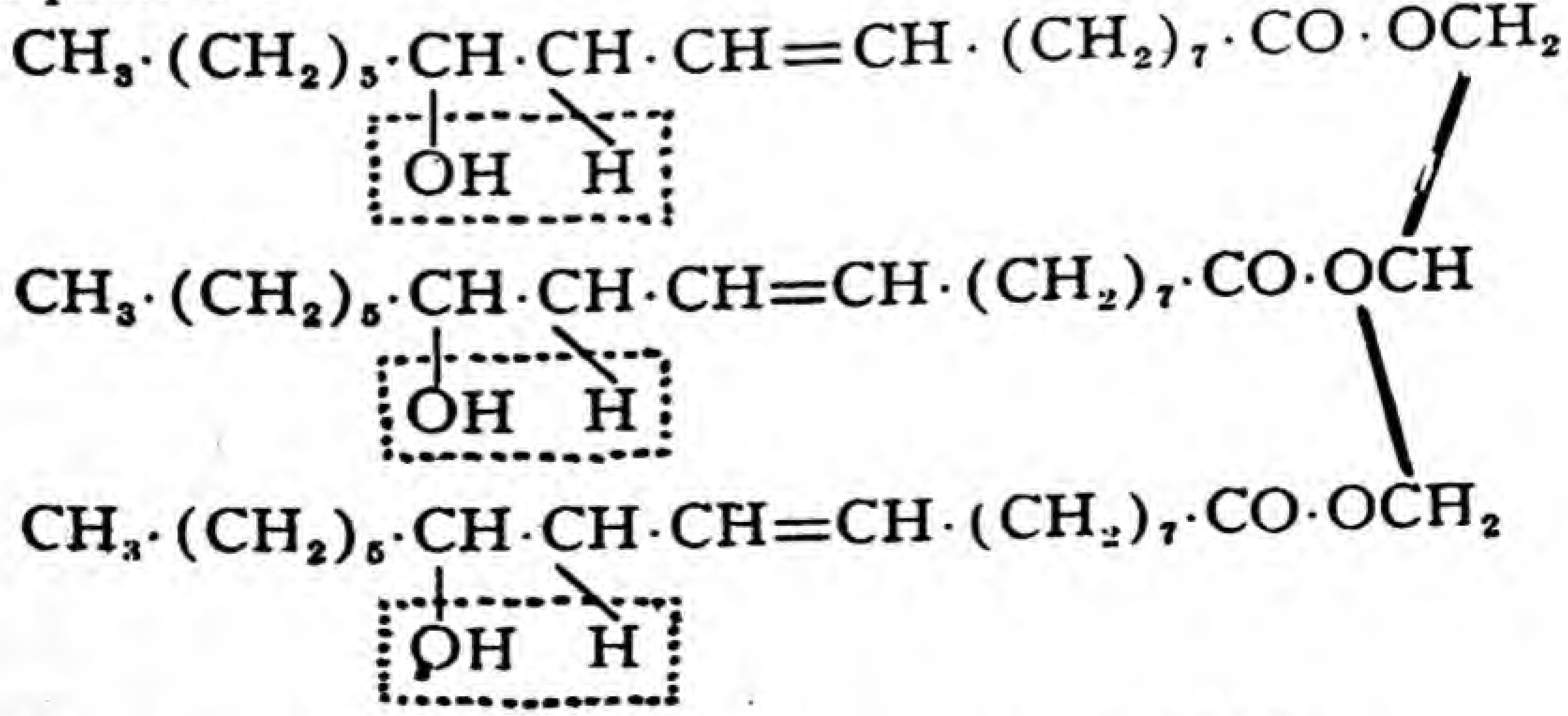
The increased speed of drying of dehydrated castor oil, over that of linseed and perilla oils, is ascribed to the presence of conjugated double bonds, which are more reactive than isolated double bonds. The conjugated portion, in dehydrated castor oil, amounts to about 25 to 30 per cent of the total.[1, 2, 3]

Analyses of natural and dehydrated castor oil:

	Natural (Merck Index)	Dehydrated (von Mikusch)
Absolute viscosity, poises	about 8*	1.6
Sp. gr. at 25°C	0.945–0.965 25/25	0.9305
Acid value	0–3*	1.8
Saponification value	179–185	190.4
Iodine value (Hanus, 400% excess)	83–88	152.0
Diene value (Kaufmann)	0–3*	21.4
Acetyl value (Andrew-Cook)	about 150*	13.5
Color (Hellige)	lighter than IL*	1–2L

* von Mikusch.

The increase of unsaturation of castor oil has been studied by von Mikusch[1] and by Forbes and Neville,[4] who tried out catalytic dehydration and catalytic dehydrogenation the first process being the more successful one. Castor oil contains a hydroxyl group and a double bond in each chain, and a conjugated system of double bonds is formed by removal of H and OH according to the following equations:


CH₃·(CH₂)₅·CH·CH·CH=CH·(CH₂)₇·CO·OCH₂
OH H
CH₃·(CH₂)₅·CH·CH·CH=CH·(CH₂)₇·CO·OCH
OH H
CH₃·(CH₂)₅·CH·CH·CH=CH·(CH₂)₇·CO·OCH₂
OH H

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[2] Bradley and Richardson: *Ind. Eng. Chem.*, 34, 237 (1942).

[3] Priest and von Mikusch: *Ibid.*, 32, 1314 (1940).

[4] Forbes and Neville: *Ibid.*, 32, 555 (1940).

The molecular weight of the triglyceride is 926, and removal of 3 H_2O corresponds to a decrease in molecular weight of 54 grams. If the hydrogen, on the 13th carbon atom of the chain, is removed, the system will contain an isolated, and less reactive, double bond.

Forbes and Neville[4] calculated the increase of unsaturation on the basis of the water expelled and the iodine number. The catalyst used was 4 per cent No. 1 Ware clay at a temperature of 230–240°C. The data obtained were as follows:

Grams of oils	Iodine No.	Theoretical H_2O, cc	Collected H_2O, cc	% increase in unsaturation On H_2O expelled	% increase in unsaturation On Iodine No.
822.0	133.2	47.9	31.0	64.7	54.2
813.0	131.3	47.4	31.4	66.3	52.0
737.3	129.7	43.0	27.0	62.8	50.2

The higher unsaturation value, obtained on the basis of the water expelled, is considered being due to new linkages not leading to unsaturation, or failure to obtain the maximum or true iodine number, a characteristic error for samples containing conjugated systems of double bonds. The authors consider that both factors may be involved.

Forbes and Neville[4] investigated a large number of catalysts for dehydration of castor oil, and their main finding was that the especially effective catalysts were clays, acid derivatives of sulfuric acid, phosphoric acid, and metallic oxides. The following table, by these authors, demonstrates the action of a variety of catalysts in dehydrating castor oil:

DEHYDRATION OF CASTOR OIL OF IODINE NUMBER 86.4 (0.1 GRAM SAMPLE)

Catalyst	Conditions °C	Conditions Min.	Iodine No.	% Increase in unsatn.	Comments
20% bentonite	230–240	45	126.4	46.3	Difficult to separate
20% kaolin	225–240	50	146.2	69.2	Difficult to separate
16% kaolin	229–235	30	149.1	72.5	Centrifuged hot
10% kaolin	230–240	30	137.7	59.4	....
4% kaolin	230–240	30	135.6	57.0	....
1% kaolin	240–250	60	129.5	49.9	....
4% White Bond clay	230–240	50	133.6	54.6	Such Clay Co.
4% No. 1 Ware clay	235–240	75	139.4	61.4	Such Clay Co.
10% (kaolin: $MgSO_4$ = 95.5)	230–240	60	129.1	49.4	Slightly cloudy
2% ($NaHSO_4$: Ware clay = 9:1)	–236	..	127.6	47.7	Dark, clear
4% Cellite	240–250	11	....	..	No water
4% pumice	–254	..	....	..	No water
10% $KHSO_4$	200–237	30	116.4	34.7	Clear, slightly darker
20% $KHSO_4$	200–223	45	117.9	36.5	....

DEHYDRATION OF CASTOR OIL OF IODINE NUMBER 86.4 (0.1 GRAM SAMPLE)

Catalyst	Conditions °C	Conditions Min.	Iodine No.	% Increase in unsatn.	Comments
5% $KHSO_4$ +	230–240	105	113.7	31.6	....
5% $KHSO_4$ (added later)	230–240	30	117.1	35.5	....
1% $KHSO_4$	240–250	30	97.8[a]	13.2	....
5% $NaHSO_4$	–240	..	127.6	47.7	Color very dark
2% $LiHSO_4$	180–185	30	122.0[a]	41.2	Color dark
2% $RbHSO_4$	–263	..	94.1[a]	8.9	Color light
4% NH_4HSO_4	250–276	80	130.0[a]	50.5	Color dark
1% $K_2S_2O_7$	240–255	60	108.1[a]	25.1	....
1% $Na_2S_2O_7$	230–250	45	132.2[a]	53.0	....
1% $Na_2S_2O_7$	240–250	60	134.9[a]	56.1	Mechanical stirrer
1% $KHSO_4$ + 1% $NaHSO_4$	240–250	50	122.7	42.0	Color lighter than with either alone
1% $NaHSO_4.H_2O$	230–250	60	132.2[a]	53.0	....
2% $NaHSO_4.H_2O$	240–253	34	135.0[a]	56.3	Color light
2% chromium acid sulfate	–250	..	....	..	No water
2% H_2SO_4 (on 2 g pumice)	150–155	12	117.5[a]	36.0	Color dark
2% H_3PO_4 (85%, on 2 g coke)	–260	..	128.1	48.2	Color fairly light
4% H_3PO_4 (85%, on 4 g coke)	230–240	11	130.5	51.0	Color very dark
4% $Al_2(SO_4)_3$	230–240	40	113.8	31.7	....
4% potassium alum powder	–260	..	110.0[a]	27.3	Color light
4% ferric ammonium alum powder	–260	..	133.8[a]	54.9	Color dark
4% $CuSO_4$	220–257	30	137.5[a]	59.2	Brown color
4% $Fe_2(SO_4)_3$	–240	..	128.0[a]	48.2	Color very dark
1% P_2O_5	250–252	6	116.0[a]	29.6	Color fairly light
2% P_2O_5	230–240	15	129.8[a]	43.4	Color dark
3% B_2O_3	–271	..	89.5[a]	3.1	....
20% Al_2O_3	–260	..	85.0	..	No water
1% Santocel (silica)	–244	..	....	..	No water
2% MoO_3	230–240	19	93.3[a]	8.0	....
2% UO_2	–260	..	....	..	No water
4% WO_3 reprecipitated powder	230–255	100	145.0	67.8	Colored product
4% Ta_2O_5	–265	..	....	..	No water
4% ThO_2	–265	..	..	..	No water
1% WO_3 reprecipitated powder	230–255	53	119.2[a]	38.0	Colored product
1% WO_3 reprecipitated powder	240–257	60	143.3[a]	65.9	Mechanical stirrer
4% WO_3 reprecipitated powder	240–250	30	148.8[a]	72.2	Mechanical stirrer
1% W_2O_5 (from expt. above)	235–265	42	127.3[a]	47.4	Mechanical stirrer
2% $AlPO_4$	–250	..	....	..	No water
2% $Na_4P_2O_7$	–245	..	....	..	No water
4% $NaH_2PO_4.H_2O$	–250	..	....	..	No water
4% CH_3COONa	–250	..	....	..	No water
1 mole BF_3	Room temp.	..	85.8[a]	..	No water
4% carbon (Darco)	–250	..	....	..	No water
4% *p*-toluene sulfonic acid	170–180	..	99.0[a]	14.6	....

[a] Iodine number obtained with 0.1 gram of sample.

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Clays are not used commercially any longer, because the resulting product is viscous and of high acid value.[7] The alkali acid sulfates, which lead to light colored products, are most widely used in the United States.[5] Dehydration of castor oil is also carried out in the presence of 0.05 to 0.1 per cent of sulfuric acid and by heating rapidly to above 260°C.[6]

---

[6] Schwarcman: U. S. Patent 2,282,892 (1942).

[7] Ufer: U. S. Patent 1,892,258 (1932).

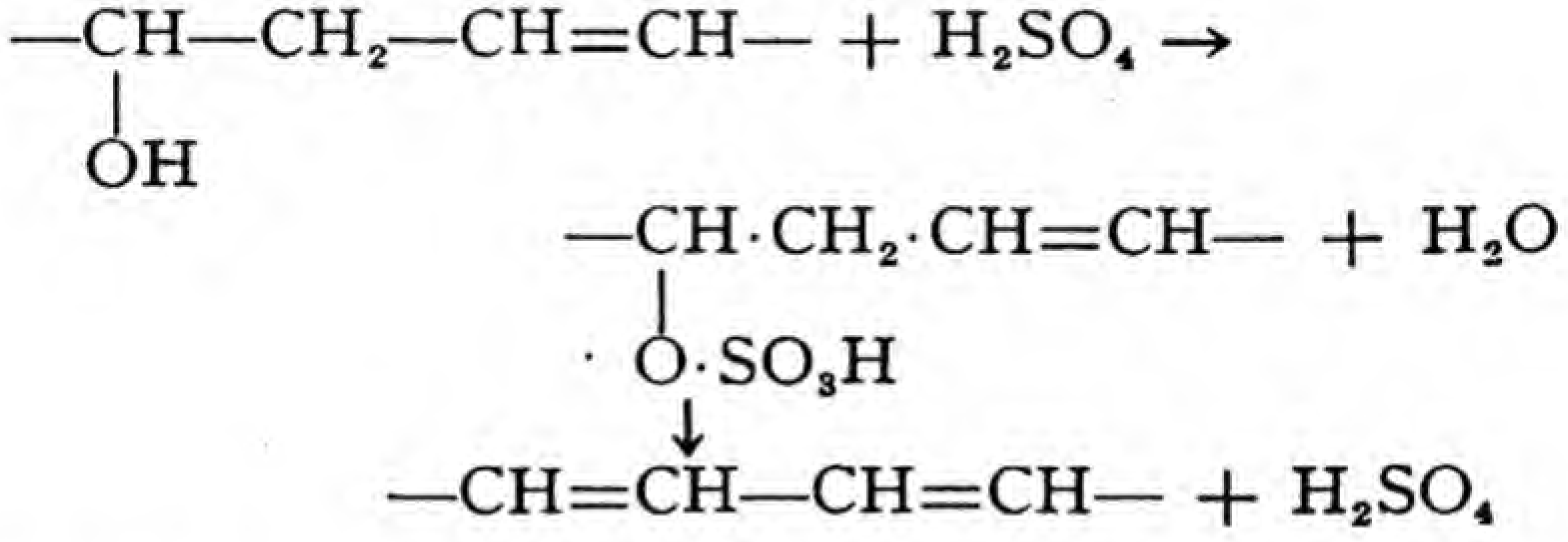
The alums and sulfates appear to owe their activity to their tendency to break down into H_2SO_4:[4]

$$Fe_2\ (SO_4)_3 + 3H_2O \rightleftharpoons Fe_2O_3 + 3H_2SO_4$$

Molybdenum oxide was moderately active and the oxide of tungsten, in the form of specially prepared $WO_3 \cdot H_2O$, was markedly active, although only after it changed to the blue W_2O_5 during the heating. The last traces of this catalyst were not readily removed from the oil. Acid phosphates were not effective. Of organic compounds, p-toluene sulfonic acid was active even at moderate temperatures (170–180°C).

The mechanism of dehydration, according to Forbes and Neville,[4] is as follows:

1) Sulfuric and phosphoric acids:



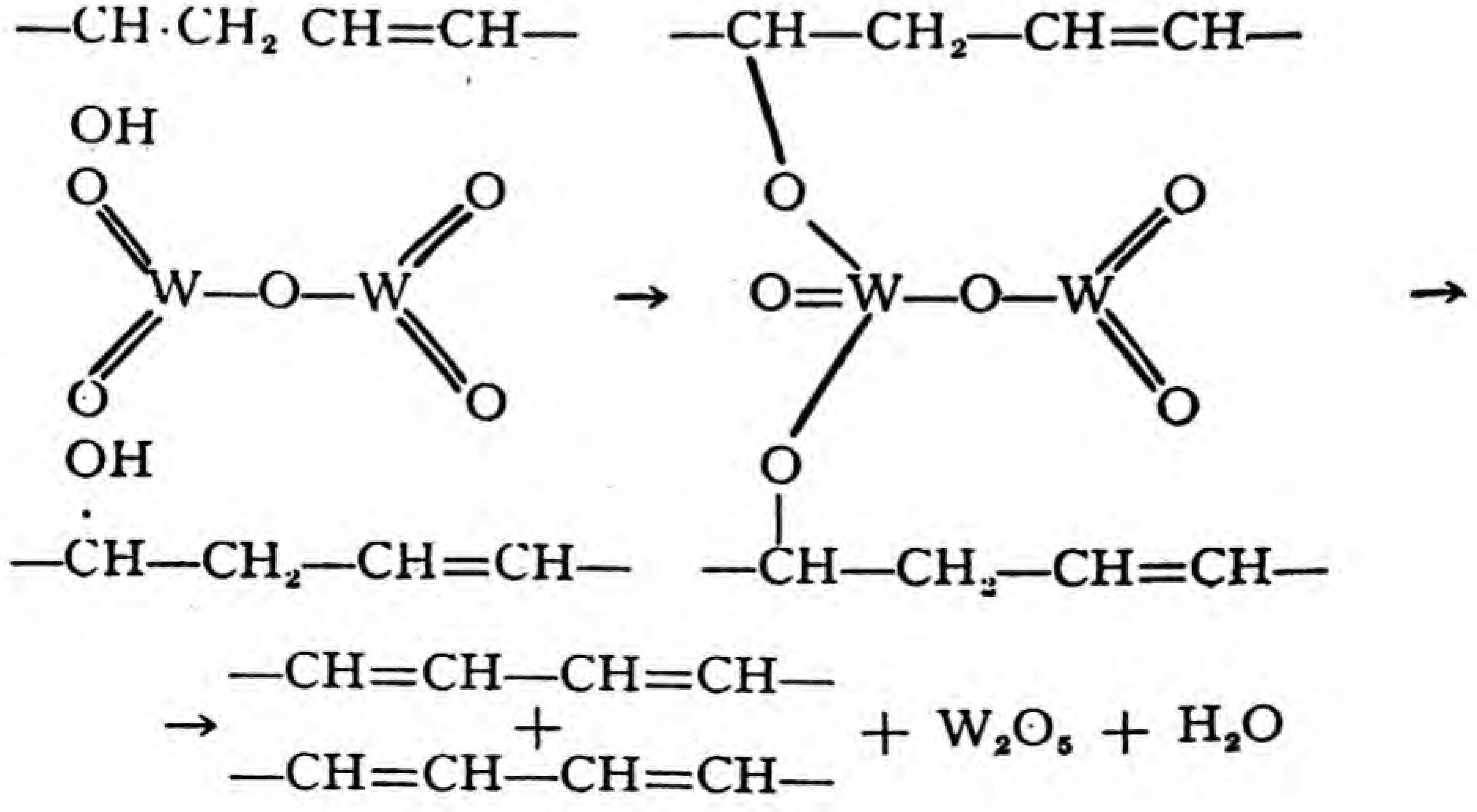
$$-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH=CH- + H_2SO_4 \rightarrow$$

$$-\underset{\displaystyle O\cdot SO_3H}{\underset{|}{CH}}\cdot CH_2\cdot CH=CH- + H_2O$$

$$\downarrow$$

$$-CH=CH-CH=CH- + H_2SO_4$$

2) Tungsten oxide (Sabatier and Mailhe):



GENERAL REFERENCE

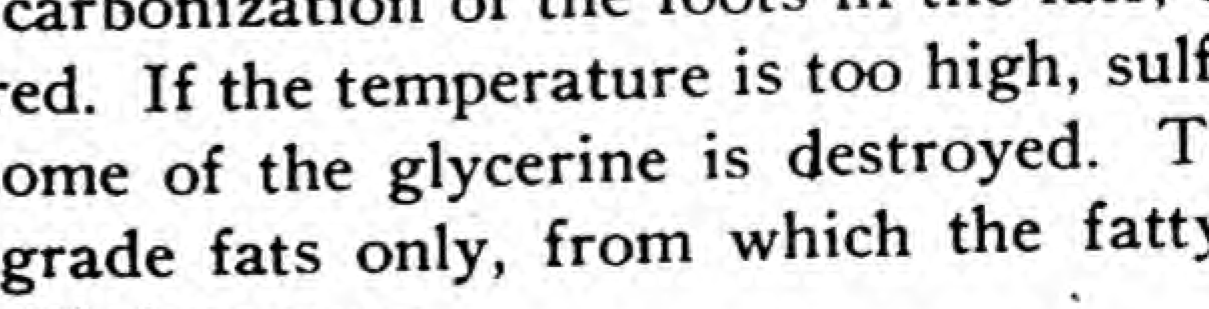
von Mikusch and Frazier: *Ind. Eng. Chem., Anal. Ed.,* 13, 782 (1941).

12. Catalytic hydrolysis of oils and fats

It is a well known fact that triglycerides, as existing in the natural oils and fats, can be hydrolyzed with water alone by using superheated steam at pressures between 250 and 300 pounds per square inch, i.e., in the temperature range of about 205 to 215°C. Fatty acids, produced this way, are dark colored. For plant practice, a process working at such high pressures is not convenient, and several catalytic agents have been used in the course of time in order to hydrolyze fats at conveniently low temperatures.

By using sulfuric acid as a catalyst, the operating temperature is as low as 110 to 130°C. Hilditch and Hall[1] claim that 5 to 8 per cent of 96 per cent sulfuric acid, at 110 to 120°C, converts a completely dry neutral fat in 8 to 12 hours. Martin[3] suggests the use of 3 to 4 per cent sulfuric acid of about the same strength at 130°C for 5 to 6 hours, the reaction scheme being:

$$C_3H_5(O \cdot CO \cdot C_{17}H_{35})_3 + H_2SO_4 + 2H_2O \rightarrow$$



$$3C_{17}H_{33}COOH + C_3H_5\begin{cases}(OH)_2 \\ O \cdot SO_2 \cdot OH\end{cases}$$

glyceryl sulfate

Due to the carbonization of the foots in the fats, the fatty acids are dark-colored. If the temperature is too high, sulfonic acids are formed and some of the glycerine is destroyed. This process is used on low grade fats only, from which the fatty acids would have to be distilled anyway.

The reaction mechanism of the acid hydrolysis has been studied by Suen and Chien[2] who hydrolyzed rape seed, peanut, lard, tallow, and whale oils with 3 to 4 per cent sulfuric acid at 100°C and determined the rate of hydrolysis. In hydrolysis of fatty oils, three different reactions are taking place (Lewkewitch): [2]

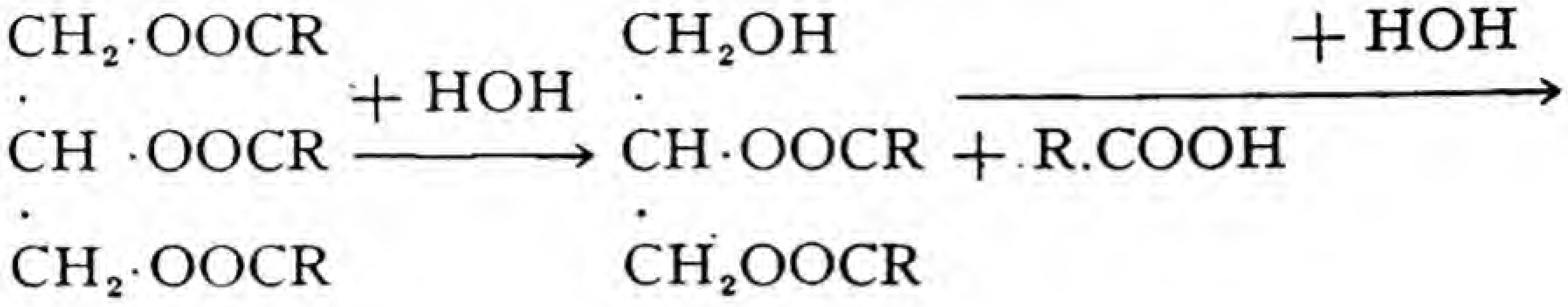
---

[1] Hilditch, T. P., and C. C. Hall: *Catalytic Processes in Applied Chemistry,* Chapman & Hall Ltd., London, 1937, p. 403.

[2] Suen and Chien: *Ind. Eng. Chem.,* 33, 1043 (1941).

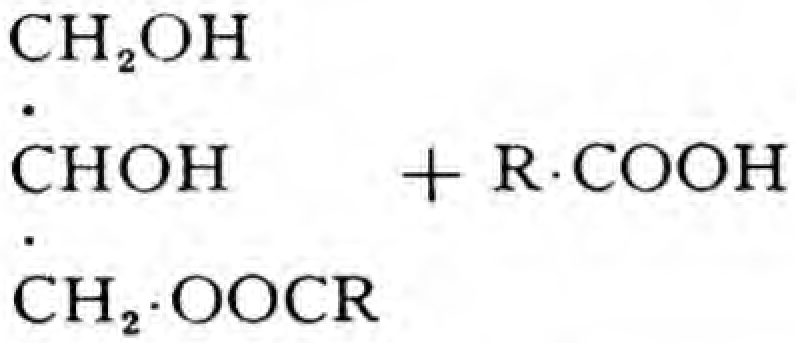
[3] Martin, G.: *Industrial and Manufacturing Chemistry, Part I,* London, Crosby, Lockwood & Son, 1920.

1.



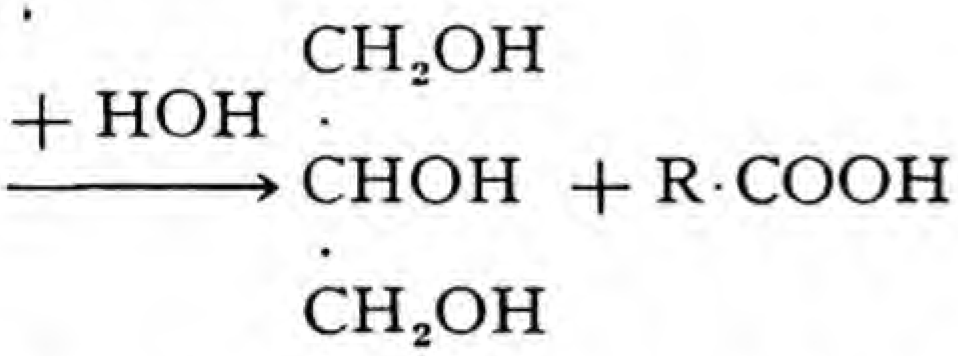
$$\begin{array}{l} CH_2\cdot OOCR \\ \cdot \\ CH\cdot OOCR \\ \cdot \\ CH_2\cdot OOCR \end{array} \xrightarrow{+\ HOH} \begin{array}{l} CH_2OH \\ \cdot \\ CH\cdot OOCR \\ \cdot \\ CH_2OOCR \end{array} + R.COOH \xrightarrow{+\ HOH}$$

2.



$$\begin{array}{l} CH_2OH \\ \cdot \\ CHOH \\ \cdot \\ CH_2\cdot OOCR \end{array} + R\cdot COOH$$

3.



$$\xrightarrow{+\ HOH} \begin{array}{l} CH_2OH \\ \cdot \\ CHOH \\ \cdot \\ CH_2OH \end{array} + R\cdot COOH$$

The observed reaction rate is the sum of the rates of these three reactions. Generally, the hydrolytic reaction can be considered as a hydrolysis of a water-insoluble ester:

$$RCOOR' + HOH \rightarrow R\cdot COOH + R'OH$$

The rate of change is then expressed by:

$$-\frac{dC_e}{dt} = k_1\cdot C_eC_wC_c$$

where C_c is the concentration of catalyst in the oil phase, C_e the concentration of ester in the oil phase, C_w is the concentration of water in the oil phase, t the time, and k a constant. C_c and C_w can be considered to be practically constant, and the rate of change is then expressed by: $-\frac{dC_e}{dt} = k_2\ C_e.$

If S is the saponification number and A the acid number of the oil, then C_e is proportional to $x = S - A$, and

$$-\frac{dx}{dt} = k_3x, \text{ from which } -\ln x = k_3t + k_4$$

where k_4 is the integration constant. The experimental data were well in agreement with these assumptions.

By using basic oxides [1,3] such as CaO, ZnO, or MgO, e.g., 1.3 per cent of lime of magnesia, calculated on the fat, and 7–10 atmospheres of steam at 176°C, the fats are hydrolyzed according to:

$$C_3H_5(O{\cdot}CO{\cdot}C_{17}H_{35})_3 + 3H_2O \rightarrow C_3H_5(OH)_3 + 3C_{17}H_{35}COOH$$

The basic oxide combines with the fatty acids and is removed by dilute sulfuric acid at the close of the conversion.

This process is usually called the autoclave-process. Hilditch [1] suggests a charge of 80 parts of fat, 20 parts of water, and 3 parts of lime alone, or of lime plus zinc dust, the latter acting partly catalytically due to its content of zinc oxide, and partly due to its content of metallic zinc, which is considered to aid in prevention of discoloration probably due to its reducing action. The charge is practically totally hydrolyzed in about 12 hours.

The reaction mechanism of autoclave splitting of fats has been studied by Lascaray,[4] who used a tallow with an acid number of 14. The rate of saponification, in the presence of sodium hydroxide as a catalyst, was increased by raising the temperature from 150 to 220°C, and by increasing the content of sodium hydroxide catalyst from 0.25 to 1 per cent (based on the fat charge). On increasing the proportion of water from 20 per cent of the fat charge to 200 per cent, the extent of the splitting, at equilibrium, increased from 75 to 95 per cent, although the rate of splitting was influenced only slightly.

With a catalyst content of combining equivalents equal to 0.5 per cent sodium hydroxide, the saponification increased in the following order: NH_4OH, NaOH, LiOH, CaO, MgO, ZnO. With mixed catalysts, the saponification rate was somewhat greater than would be calculated from the activity of the individual components.

---

[4] Lascaray: *Fette u. Seifen*, **46**, 628 (1939); *Chem. Abstracts*, **34**, 8313 (1940).

It was concluded that the saponification of the fat is a homogeneous reaction taking place in the fat phase between the fat and the water dissolved in it. The basis for this conclusion was the observation that the maximum saponification rate occurs under conditions unfavorable to formation of the emulsion, and the activity of the catalyst increases in the order of the lyotropic series and with growing ability of the catalysts to increase the solubility of water in fat acids.

An ingenious process, for hydrolyzing neutral fats and oils, was discovered by Twitchell[5] (1900), who found that emulsifying agents of sulfuric acids had hydrolytic properties. Twitchell treated a mixture of oleic acid and benzene with a large excess of concentrated sulfuric acid. An excessive rise in temperature was avoided by cooling the mixture, and by adding the acid slowly. After several hours, the reaction was practically complete, mainly according to:

$$C_6H_6 + C_{18}H_{34}O_2 + H_2SO_4 \rightarrow \underset{\text{benzene stearosulfonic acid}}{C_6H_4(SO_3H)C_{18}H_{35}O_2} + H_2O$$

Similarly, using naphthalene or phenol instead of benzene, Twitchell prepared naphthalene stearosulfonic acid: $C_{10}H_6(SO_3H)C_{18}H_{35}O_2$; and phenol stearosulfonic acid: $C_6H_3OH(SO_3H)C_{18}H_{35}O_2$. Since then, similar preparations have been made such as cymene stearosulfonic acid;[6] octahydro anthracene sulfonic acid (Idrarapid); 1-isopropyl-, butyl-, or other alkyl-, naphthalene sulfonic acid (Nekal); hydrogenated castor oil acids sulfonated with naphthalene (Pfeilring), and a sulfonated fraction from petroleum refining (Kontaktspalter).[7,8] The purpose of these experiments was the production of a lighter colored product of fatty acids.

---

[5] Twitchell: *J. Am. Chem. Soc.*, **22**, 22 (1900).

[6] McKee and Lewis: *Chem. Met. Eng.*, **24**, 969 (1921).

[7] Bean, H. K.: *Utilization of Fats*, New York, Chemical Publishing Co., 1938.

[8] Pickering: *J. Soc. Chem. Ind.*, **44**, 242T (1925).

The Twitchell agent is washed free from the sulfuric acid before use. The foots, in the fat to be hydrolyzed, are destroyed by boiling with sulfuric acid. To 100 lb of oil 40 to 100 lb of distilled water and 0.5 to 1 per cent of the Twitchell agent are added. The mixture is kept boiling by means of steam blown through it, and after an induction period, the hydrolysis takes place with substantial velocity, the rate being proportional to the concentration of neutral fat present. The full hydrolysis requires 12 to 60 hours. Half way through the period, needed for hydrolysis, the aqueous glycerine layer may be drawn off and replaced by fresh water for shortening the time of conversion.

In order to avoid dark-colored fatty acids, air should not have access to the mixture during hydrolysis. The conversion is practically complete, 97 to 98 per cent.

The aromatic part of the Twitchell agent combines with the fat in the mixture being hydrolyzed, and the sulfonic group is oriented toward the water. It is the presence of this strongly acidic group that causes hydrolysis.[1, 9, 10]

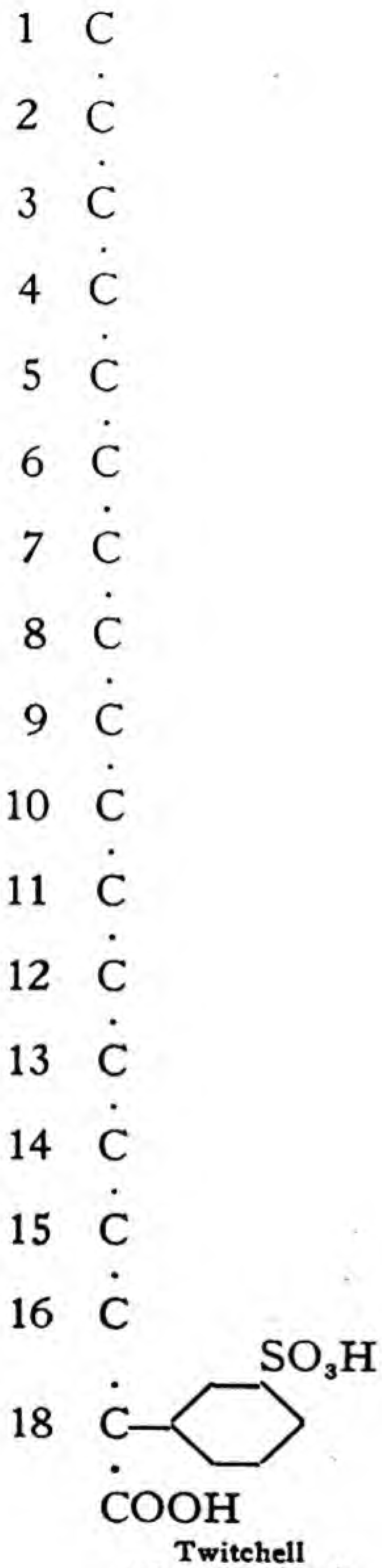
In a study on the influence of adding various substances to differently prepared Twitchell reagents (Idrapid, Pfeilring, Kontakt),[11] it was found that by adding one per cent solutions of hydrochloric acid, sulfuric acid, formic acid, oxalic acid, sodium sulfate, sodium bisulfate, and sodium chloride, the action depended chiefly on whether or not the reagent was salted out. Idrapid is difficult to salt out and showed considerable increase in emulsification in the presence of increasing amounts of strong electrolytes. For the readily outsalted Kontakt reagent, the emulsification increased strongly in the range of small electrolyte concentrations.

---

[9] **Goldschmidt, F.:** *Seifensieder-Ztg.*, **39**, 845 (1912); *Z. angew. Chem.*, **26**, 134 (1913).

[10] **Grimlund:** *Ibid.*, **25**, 1326 (1912).

[11] **Nishizawa:** *J. Soc. Chem. Ind. (Japan)*, Suppl. **31**, 291B (1928).


1 C
2 C
3 C
4 C
5 C
6 C
7 C
8 C
9 C
10 C
11 C
12 C
13 C
14 C
15 C
16 C
SO₃H
18 C
COOH

Twitchell reagent molecule

Weak acids do not salt out the Twitchell agent and influence the emulsification very little. The presence of sodium salts and glycerin slightly increases the emulsification. The influence of the concentration of the Twitchell reagent itself is not considerable.

Fats can also be split by heating the glycerides with absolute alcohol (methyl alcohol best) containing one to two per cent hydrochloric acid (alcoholysis):[12]

$$C_3H_5(COOR)_3 + 3R'OH \rightarrow$$
$$C_3H_5(OH)_3 + 3RCOOR'$$

This reaction is facilitated by the use of a neutral solvent such as naphtha or carbon tetrachloride. This method is applicable in practical work if the methyl or ethyl esters of the fatty acids are desired, and the method is used analytically.

Formation of Carboxylic Acids

Mention should also be made of the work by Vail[1] and Carpenter[2] on the formation of carboxylic acids by reacting olefins, steam and carbon monoxide over proper catalysts, the resulting carboxylic acid having one more carbon atom than the olefin in the reaction mixture. This reaction is catalyzed by the presence of hydrogen halides and activated carbon or charcoal, the latter being treated with a third catalytic substance, e.g., phosphoric acid, boric acid, silico-tungstic acid, boron phosphate, metallic halides, etc. Inert gases such as nitrogen, methane, or carbon dioxide may be added to the mixture in order to better control the exothermic reaction. The reaction is supposed to proceed according to the following reaction scheme when reasonably pure starting materials are used:

$$RR_1C{=}CR_2R_3 + H_2O + CO \rightarrow CHRR_1CR_2R_3\cdot COOH$$

the reaction with ethylene being:

$$C_2H_4 + H_2O + CO \rightarrow CH_3CH_2\cdot COOH$$

A typical example is as follows:[2]

"A gaseous mixture, containing by volume 90 parts carbon monoxide, 5 parts ethylene, and 20 parts steam, is passed together with approximately 5 parts hydrogen chloride into a conversion chamber containing a zinc chloride catalyst on activated charcoal. The catalyst is prepared by saturating the activated charcoal with a solution of zinc chloride of sufficient concentration to give a charcoal containing approximately 20 per cent by weight of zinc chloride. The catalyst chamber is designed for carrying out exothermic gaseous reactions and the temperature is maintained therein at approximately 325°C while the pressure is held at approximately 700 atmospheres. The condensate obtained upon cooling the converted gases will give a good yield of aliphatic carboxylic acid containing a high percentage of propionic acid."

---

[12] Holde, D.: *The Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes, 2nd Ed.*, New York, John Wiley & Sons, Inc., 1922.

[1] Vail: U. S. Patents 1,895,238 (1933) and 1,924,764 (1933).

[2] Carpenter: U. S. Patents 1,924,763, 1,924,766, 1,924,767, 1,924,768, 1,924,769 (1933) and 2,008,348 (1935).

According to this work, formic acid is produced from carbon monoxide and steam in the vapor phase, over boron phosphate or a halide of an alkali or alkaline earth as catalyst at around 325°C and 700 atmospheres pressure.

AUTHOR'S INDEX

Abbott, 324
Abel, 24
Abell, 320
Aboulenc, 92
Acker, 308
Adadurov, 124, 147
Adams, 166, 227, 235
Adams, K. S., 339
Addicks, 132
Adkins, 96, 97, 98, 112, 131, 145, 219, 220, 221, 223, 224, 226, 227, 228, 229, 230, 231, 232, 233, 234, 292, 351, 410, 412
Akerlöf, 73
Akulov, 47
Albertsen, 235
Allison, 340
Almquist, 311
American Instrument Company, 96
American Petroleum Institute, 367
Anderson, 235, 295, 377
Andrew, 128, 199
Andrews, 62, 243, 326
Andrieth, 294, 295
Andrussov, 317, 321
Anglo-Iranian Oil Co. Ltd., 377
Anisimov, 149, 208, 209
Anschutz, 252
Anzai, 402
Archer, 148, 218
Arents, 129
Armfield, 195
Armstrong, 10, 16, 92, 184, 343
Arrhenius, 73, 105
Ashdown, 275
Ashton, 123, 133, 135, 139, 149
Aston, 261, 262
Atack, 141
Attapulgus Clay Company, 182
Audibert, 341, 342

Babad, 320
Backhaus, 129
Bäckström, 37, 189, 197
Badische Anilin-und Sodafabrik, 7, 8, 236, 329
Baekeland, 269
Bahr, 101, 147, 169
Bahr and Bahr, 101
Bailey, 52, 142
Baily, 36
Baker, 284, 306
Baker & Co., Inc., 162, 163, 164, 165, 168, 169
Balandin, 58, 83, 99, 120, 158, 234
Balaty, 294
Ballard, 377
Balz, 204
Bancroft, 55, 99, 111
Barker, 13, 130
Barnes, 19
Barr, 361
Basset, 308, 311, 324,
Bataafsche, N. V. de, Petroleum Mataschappij, 149
Baudisch, 189
Baxter, 51
Bayer, 286
Bayley, 58
Beamer, 347
Bean, 420
Beck, 190
Beckers, 243
Beckmann, 235, 311
Beeck, 33, 58, 101
Behnke, 183
Beindl, 148
Bell, 81, 286
Bennet, 135
Benton, 310
Bergius, 126, 219, 348, 353
Berkmann, 53, 54, 170, 176, 256, 257, 372, 388
Berl, 192, 306, 357
Berry, 253
Berthelot, 246, 307, 328
Bertsch, 142, 143, 174
Berzelius, 4, 6

Beyer, 346
Biebesheimer, 357
Bielouss, 251
Bigelow, 36
Biltz, 120, 187, 327
Birch, 253, 259, 282
Bittler, 204
Bjerrum, 9
Bladger, 130
Blanck, 410
Blick, 306
Bliss, 236
Bloch, 374
Blom, 323
Bode, 320
Bodenstein, 18, 43, 48, 87, 108, 119, 305, 306, 317, 324
Boese, 244
Bolton, 401
Bond, 135
Bondonneau, 324
Bone, 128, 199, 326
Boner, 324
Bonnel, 220
Booge, 62
Boriskoff, 227
Bosch, 6, 48, 127, 150, 190, 312
Boswell, 58, 136, 154, 251, 253
Bouchardat, 324, 384
Bougult, 288
Bouton, 142
Bouveault, 410
Bowden, 91
Bowe, 73
Bowles, 93, 94, 358
Boyd, 37
Bradley, 20, 21, 22, 158, 263, 291, 413
Brauer, 139
Bray, 139, 172, 194
Bredig, 54, 189, 242, 321
Bridgewater, 386
Briggs, 138
Briner, 305, 320
British Fuel Research Board, 354
Brochet, 253
Brode, 19
Brönsted, 9, 35, 71, 73, 74, 240, 261
Brooke, 237
Brown, 140, 141, 172, 178, 182, 189, 237, 244, 249, 287, 324, 341, 361, 364, 365, 366, 368
Brownlee, 272, 273
Bruckner, 130, 140
Brugger, 183
Brunauer, 31, 32, 35, 38, 109, 324
Brunn, 151
Brunner, 89, 189, 275
Bruson, 275
Buchan, 272
Burbidge, 249
Burdick, 306
Burgin, 207
Burk, 99, 136, 149, 257, 275
Burke, 196, 386
Bursian, 43
Burwell, 243
Busse, 307
Buzag, 35
Byrns, 267, 291

Cadenhead, 324
Calcott, 218
Calingaert, 146
Cambron, 339
Canneri, 144, 202
Carbon Chemicals Corporation, 395
Caro, 190, 319, 322
Carothers, 166, 286, 386
Carpenter, 423
Carpmael, 236, 344
Carter, 346
Casale, 314
Cattelain, 288
Centnerszwer, 193
Chabrier, 288
Chance, 7
Chapman, 327
Chappel, 246
Chariton, 66
Chemical and Metallurgical Engineering, 390, 395
Chertov, 291
Chien, 417
Chilton, 191, 316
Choppin, 148
Christiansen, 37, 43, 61, 70, 106
Clark, 130
Claude, 313
Claus, 7
Clement, 4, 6, 191
Clough, 347
Clusius, 67, 68, 69, 105, 148
Cohen, 250, 347
Coley, 211

Collins, 386
Colson, 132
Connor, 145, 223, 228, 230, 233, 412
Conover, 203
Consolidated Engineering Corporation (The), 21, 23
Constable, 207
Corson, 256
Coutelle, 385
Covert, 223, 228
Cowan, 149
Cozzi, 144, 149, 202
Crafts, 252, 287
Cramer, 390
Craver, 203
Crawford, 405
Craxford, 339
Crittenden, 30
Cronheim, 187
Curme, 252, 284
Curtis, 191, 315

Dakin, 250
Daniels, 307
Daudier, 205
Davidson, 134, 180
Davis, 163, 235
Davy, 6, 99, 192
Dawson, 70, 73, 74, 77
Day, 131, 202
Deacon, 7, 193
Deane, 266
Dee, 135
Deem, 402
Defense Plant Corporation, 395
Delfino, 347
Demme, 321
De Simo, 129, 206
Desormes, 4, 6, 191
Deutsche Gold-und Silberscheideanstalt A.-G., 327, 345
Dhar, 38, 46, 320
Dickinson, 148
Dieckmann, 236
Dilworth, 136
Dimroth and Schmoedel, 287
Diworky, 112
Dobychin, 156
Dodge, 236, 261, 342
Doehereiner, 4, 6
Dohse, 105
Douglas, 284
Doumani, 267
Dovgelewitch, 257
Downs, 203, 204
Dreyfus, 244, 248
Dryer, 52
Dufraisse, 52, 108
Dulong, 6
Dunstan, 253, 259, 282
Du Pont de Nemours, I. E., and Co., Inc., 145, 206, 304
Durand, 320
Dutton, 254
Dvinyaninova, 409
Dymock, 347

Edgar, 146
Edlund, 362
Egerton, 108
Egloff, 52, 53, 54, 109, 116, 170, 176, 256, 257, 261, 262, 264, 338, 339, 360, 372, 373, 374, 377, 382, 388
Eichelberger, 263
Eisenhut, 25
Elgin, 289
Elkin, 134
Elkington, 343, 347
Ellis, 159, 269, 284, 402
Elöd, 321, 329
Emmett, 31, 32, 58, 93, 109, 150, 182, 222, 234, 309, 310, 324
Engelder, 141
Eoff, 346
Erdmann, 324
Ernst, 315
Euler, 62, 299
Evan and Imperial Chemical Industries Limited, 141
Evans and Albertsen, 235
Evell, 236
Ewell, 329
Ewing, 180

Faraday, 5
Farbenfabriken vorm. F. Bayer, 8
Farkas, 182
Farkas and Farkas, 282
Farlow, 223, 227, 231
Fauser, 314, 319, 321
Fehér, 134
Fellinger, 294
Fenske, 132, 134, 182, 219, 341, 342, 411
Fieldner, 341

Filtrol Corporation, 180
Findlay, 82
Fink, 87
Fischbeck, 111
Fischer, 128, 151, 159, 169, 170, 199, 266, 329, 330, 336, 339, 340, 359, 366, 368, 390
Fitch, 12
Flamenol, 391
Florentin, 349
Fogler, 319
Folkers, 145, 233, 289, 412
Forbes, 413, 414, 416
Foster, 182
Franck, 190, 196, 319, 322
Frankel, 242
Frankenburger, 46, 63, 102, 150, 183, 300, 309
Fraser, 8, 128, 135, 159, 172, 173, 234
Frazer, 194
Frazier, 416
Frebault, 224
Freudenberg, 246
Friedel, 252, 287
Frolich, 132, 134, 182, 200. 339, 340, 341, 342
Fromherz, 148
Fuchs, 321, 347
Fuller, 284
Fulton, 321

Gabriel, 268
Gallay, 384
Galloway, 341
Gantz, 148
Gapon, 90
Gardner, 251
Gasol, 160
Gee, 275
General Chemical Co., 316
Genthe, 39, 204
George, 194
Gibbs, 8, 203
Gibbs, H. D., 203
Gibson, 64
Gilman, 129
Gilmore, 93, 94, 358
Ginell, 280
Glasstone, 81, 85
Gluud, 235
Gmelin, 124, 167, 306, 319
Gohr, 361, 364, 365, 366, 368
Golden, 339
Goldschmidt, 421
Gordon, 348
Graesser, 286
Graham, 354
Graves, 207, 344
Green, 36, 40, 324
Greenwood, 93
Griffith, 83, 91, 291
Grignard, 182, 252
Grigoryan, 158
Grills, 141
Grimlund, 421
Grob, 110
Groggins, 286, 294
Groll, 136, 177, 207, 208
Groombridge, 135
Grosse, 205, 206, 215, 255, 375
Grüen, 196
Gruenstein, 8
Guenther, 287
Gutehoffnungshütte Oberhausen A.-G., 204

Haas, A.-G., 249
Haber, 6, 43, 93, 111, 148, 189, 198, 307, 308, 310, 324
Hadman, 67, 148
Haensel, 382
Hahn, 127, 128, 204
Halban, 76
Hale, 209
Hall, 8, 139, 142, 192, 343, 349, 353, 403, 405, 412, 417
Hamilton, 232
Handford, 191, 319
Hanford, 347
Hansenclever, 193
Hansford, 222
Hantsch, 324
Hara, 130
Harbeck, 109
Harden, 299
Harned, 73
Harries, 289, 384
Harris, 222
Harrison, 62
Hasche, 306
Hawk, 199
Hayek, 320
Heath, 324
Hedges, 113

Hedley, 342
Hellrung, 300
Henke, 140, 141, 182
Heraeus Company, 165
Herington, 339
Herzfeld, 61, 66
Hicks, 151
Hilditch, 8, 92, 139, 142, 192, 263, 343, 349, 353, 403, 404, 405, 412, 417
Hill, 295
Hilley, 150, 222
Hinshelwood, 18, 42, 43, 47, 62, 63, 64, 67, 69, 70, 76, 109, 148, 241, 304, 305, 308, 324
Hirst, 359
Hodgeman, 123
Hoffmann, 169
Hofmann, 385
Holde, 423
Holm, 237
Holmboe, 407
Hoog, 213
Horrex, 262
Hougen, 235
Hovey, 273,
Howk, 343
Huber, 101
Huffmann, 106, 266
Hughes, 241
Hulla, 262, 264, 382
Humble Oil and Refining Co., 377
Hurd, 127
Hurt, 34
Hurter, 7, 193
Hutschenreuter, 300
Huttig, 134, 182

Ibing, 336, 337, 338
I. G. Farbenindustrie A.-G., 130, 140 158, 172, 190, 235, 348
Iler, 154
Immendorf, 252
Imperial Chemical Industries, 316, 348
Industrial and Engineering Chemistry, 391, 392, 393, 394
Ingold and Wasserman, 182
Institution of Automotive Engineers, Australia, 382
Ipatieff, 2, 5, 18, 48, 56, 130, 136, 141, 154, 170, 171, 172, 182, 205, 206, 210, 211, 219, 225, 242, 243, 253, 255, 256, 257, 258, 264, 267, 269, 280, 281, 282, 292, 327, 348, 349, 373, 375, 382
Ivannikov, 248

Jacob, 128, 160, 246
Jaeger, 142, 174, 191, 192, 203
Jakowlew, 225
James, 196, 204
Jamieson, 397, 405
Jander, 110
Jant, 199
Jenkins, 327
Job, 125, 188
Johns, 347
Johnson, 132, 148, 207, 251, 322, 341
Johnston, 307
Jones, 130, 340
Jordan, 75
Jorrissen, 109
Joshua, 347
Jost, 197
Jungers, 309
Jungfleisch, 328
Jutteman, 300

Kao, 144
Kassel, 212, 305, 307
Kassler, 182
Kather, 222
Kato, 138
Katz, 204, 275
Kaufmann, 227
Kaveckis, 402
Kawai, 140
Kazanskii, 217
Keenan, 324
Kekulé, 262
Kelber, 55, 77, 196, 197
Kendall, 62, 75
Kenner, 287
Kenrick, 16
Ker, 391
Ketoid Co., The, 244
Keunicke, 103, 111
Key, 73
Keyes, 237
Keys, 246
Kharasch, 148, 251, 287
Kienle, 273
Kiliani, 188
Kimbal, 106
King, 360

Kino, 138
Kirby, 148, 386
Kirchoff, 4, 6
Kirsch, 76
Kissling, 204
Kistiakowsky, 183, 234, 286
Kistler, 179
Kivinen, 239
Klemenc, 320
Klima, 320
Kling, 349
Knietch, 7, 162, 191
Knoevagel, 287
Knox, 249
Knuth, 396, 403, 404
Koch, 151, 336, 337, 338, 387
Koenigs, 254
Koerter, 357
Koertmann, 321
Kohlschütter, 132
Komarewsky, 211, 253, 261
Kondakoff, 384
Kondarev, 182
Konig, 324
Konrad, 25
Kothrock, 339
Krasheninnkova, 209
Kreskov, 144
Krieble, 79
Kroenig, 129
Kröger, 104
Krüger, 249
Kuhlmann, 5
Kummer, 310
Kunsman, 310, 311
Kurbatov, 95, 257
Kuss, 111, 309

Lamb, 172, 194
Landis, 322
Lang, 199
Lange, 123, 130
Langenbeck, 236, 238, 300
Langmuir, 25, 27, 28, 29, 84, 85, 308
Larson, 147, 195, 315, 322
Lascaray, 419
Lauer, 286
Laupichler, 95
Lautenschläger, 284
Lavoisier, 4
Lazier, 100, 131, 145, 146, 246, 343, 403, 410
L'Azote, Inc., 199
Lebedev, 384
Le Clerc, 82, 123
Lee, 291
Lefebvre, 123
Lehrman, 16
Leibig, 186
Lenher, 87
Leontovitch, 264
Lepsoe, 138
Le Rossignol, 310
Lessing, 339
Levey, 339
Lewis, 341, 420
Lewis (Judd), 12
Lewkewitch, 418
Liberman, 217
Liddel, 19
Liljenroth, 193
Lindenbaum, 189
Linder, 346
Linhorst, 306
Linstead, 219, 235
Lippert, 204
Litkenhous, 222
Lloyd, 241
Loder, 151
Loew, 7, 165, 187
Lohse, 2, 12, 62, 90, 91, 101, 140, 151, 168, 172, 265, 276
Long, 234
Lonza Elektrizitätswerke und chem. Fabriken A.-G., 320
Love, 324
Lowry, 52, 71, 75, 77, 79, 80
Lunge, 109, 192, 306
Lush, 347, 401
Lyons, 291

Macaluso, 112
Mack, 248
Madenwald, 141
Mailhe, 150, 205, 249, 292, 412, 416
Makray, 354
Malishev, 254, 377
Mann, 222
Marek, 128, 204
Mark, 75, 386
Martin, 16, 167
Martin, G., 407, 417
Mascu, 248

Mathes, 294
Matov, 48
Mattox, 215
Mautner, 140
Mavity, 206
Maxted, 56, 57, 100, 401
Mayo, 286
McAllister, 142, 280, 282, 283, 377, 382
McArthur, 135
McCutcheon, 405
McKee, 252, 420
McLaughlin, 251, 253
Mears, 286
Medsforth, 49
Megson, 272
Meighan, 340
Mellor, 153
Menschutkin, 246
Mensel, 169
Messner, 102, 183, 309
Metasap Chemical Co., 135
Metzger, 347
Meyer, 75, 159, 222, 329
Miayake, 402
Michaelis, 295
Michel, 82
Michell, 123
Midgley, 37, 38
Mignonac's method, 231
Mikusch, von, 412, 413, 415, 416
Milas, 199
Milligan, 246, 253, 396, 403, 404
Mills, 138
Milner, 190
Miner, 272, 273
Mitchell, 183
Mitcherlich, 5, 6
Mittasch, 6, 10, 48, 98, 103, 111, 150, 170, 171, 190, 204, 298, 309, 310, 311, 312, 329, 340
Moelwyn-Hughes, 76
Moeser, 189
Moissan, 2, 153, 322, 324
Moldawsky, 215
Moldenhauer, 313
Molstad, 342
Montagnes, 339
Moore, 148, 263, 403
Morey, 244, 248
Morgan, 339, 342
Morozov, 89
Morrell, 52, 53, 54, 109, 116, 170. 176, 206, 215, 256, 257, 360, 372, 374, 388
Morris, 138, 222
Moscow conference on heterogeneous catalysis, 109
Moshier, M. B., 138
Moshier, R. W., 138
Mott-Smith, 59
Moureu, 52, 78, 108
Mozingo, 289
Mueller, 298
Muffling, 197
Muhlert, 323
Mullen, 248
Muller, 3, 321
Mumm, 241, 327
Murat, 222
Murphree, 361, 364, 365, 366, 368
Murphy, 390
Musgrave, 304
Mustone, 391
Myers, 113

Nagel, 304
Nark, 183
Naumann, 127
Nedelmann, 329
Nelson, 220
Nernst, 43, 89
Neumann, 128, 160, 189
Neville, 413, 414, 416
Newling, 241
Nieuwland, 235
Niewenburg, 192
Nishizawa, 421
Noller, 254
Nooijer, 192
Nord, 183
Normann, 7, 233, 397
Norrish, 69
Norton, 148, 270, 275, 276
Noyes, 89
Nuodex Products Co., Inc., 135
N. V. de Bataafsche Petroleum Maatschappij, 183, 346
N. V. Int. Koolwaterstoffen Maatschappij, 151
Nyrop, 183, 354

Orloff, 349
Orlow, 242, 292
Osborg, 129
Ostromilansky, 384

Ostwald, 5, 6, 7, 10, 113, 190, 319
Ott, 183

Paal, 166
Palmer, 207, 241
Pardee, 261
Pardubitzer Fabrik der Aktiengesellschaft für Mineralöl-Industrie, vorm. David Fanto and Co., 196
Parks, 204, 227, 362
Parmentier, 4, 6
Parodi-Delfino, 347
Parr Instrument Company, 97
Parsons, 191, 317
Partington, 316, 317
Passins, 148
Pasteur, 5, 295
Patart, 339, 347
Patrick, 147
Patterson, 202
Paul, 150, 222
Pease, 43, 130, 222
Peisakhov, 291
Petrow, 242, 292
Phillips, 191
Pickering, 420
Pidgeon, 108
Pier, 360
Pierce, 227
Pietch, 95, 125
Pines, 255, 256, 269, 280
Pistor, 127
Pitzer, 173, 194, 205
Plant, 291
Platonov, 149, 208, 209
Podelt, 48
Polányi, 64, 241
Pollak, 320
Polyakov, 318
Polzenius, 7
Porocel Corporation, 181
Prahl, 294
Priest, 413
Pufahl, 235
Pyzhev, 310

Querfurth, 347
Quiggle, 132, 182, 342

Radley, 238
Radzievanowskii, 261
Raineau, 341, 342
Rakitin, 225
Rampine, 183
Raney, 158
Raschig, 7, 193, 203, 306, 323
Razuvaev, 267
Read, 287
Reich, 125
Reichel, 215
Reid, Emmet, 5, 19, 36, 52, 77, 101, 183, 184, 196, 204, 209, 217, 222, 242, 243, 244, 246, 253, 256, 275, 276, 288, 329, 348, 397
Reinacker, 172
Reinhardt, 284
Reitstötter, 139
Remy, 118
Reppe, 135
Reyerson, 222
Reynhart, 347
Rheiner, 286
Rhenania Verein chemischer Fabriken, 327
Rice, 14, 16, 39, 60, 62, 66, 77, 78, 348
Richardson, 20, 21, 22, 396, 403, 404, 413
Richter, 111, 403
Rideal, 8, 32, 39, 91, 100, 101, 194, 207, 275
Ridsdale, 401
Riegel, 328, 341
Roberts, 136, 177, 207
Robertson, 37, 194
Rock, 21
Rodinov, 266
Roebuck, 4
Rogers, 52, 53
Roginskii, 18, 37, 183
Röhm, 249
Rohrmann, 197
Rojahn, 129
Roman, 235
Rooney, 327
Ross, 377
Rossini, 19
Rothen, 324
Rowe, 235
Rudisill, 141
Ruff, 140
Rumeau, 107
Rush, 409
Russell, R. P., 361
Rusznyák, 133
Ruzika, 218

Sabatier, 5, 36, 128, 130, 136, 150, 184, 204, 205, 207, 209, 217, 219, 221, 222, 224, 242, 246, 249, 250, 288, 292, 329, 343, 348, 397, 416
Salls, 252
Sapper, 7
Sauer, 410
Sauter, 81
Scal, 324
Scalione, 194
Schaad, 327
Schenck, 233
Schlingman, 273
Schmid, 24
Schmidt, 124, 131, 228, 229, 235, 299, 320, 350
Schoenbein, 6, 46, 186
Schoenberg, 129
Schneider, 235, 329
Scholl, 217
Schrauth, 233
Schulten, 129
Schultes, 304
Schultze, 326, 385
Schulz, 280
Schumacher, 48, 60, 305, 307
Schwab, 8, 42, 82, 111, 304
Schwarcmann, 415
Scott, 142, 295
Seer, 217
Semenoff, 66
Semenov, 43, 280
Senderens, 92, 128, 205, 207, 222, 224, 243, 343
Senter, 54
Seregienko, 207
Seuferling, 95
Shell Chemical Company, 367
Shell Development Company, 206, 367, 370, 371, 376, 378, 382, 383
Sherlock, 237
Shiffler, 237
Shoenbein, 187
Shreve, 248
Shriner, 166
Shute, 180
Sieck, 152
Sieverts, 124
Signaigo, 227
Siller, 134
Simla, 280
Simon, 250
Simonds, 135, 148
Simons, 218, 279
Simpson, 286
Skau, 234
Skinner, 354
Skita, 166, 169, 222
Skrabal, 72, 75, 239, 241
Slansky, 196
Smith, 33, 58, 69, 101, 139, 291, 341
Snow, 237
Socony-Vacuum News, 180
Solvay Process Co., 316
Sorokin, 43
Spence, 8, 82, 111
Sperry, 235
Spilker, 253
Spoehr, 188
Sprague, 230
Sprenger, 307
St. Gilles, 246
Stamm, 110
Standard Oil Company of New Jersey, 349
Standard Oil Development Company, 361, 362, 364, 365, 368, 378
Stanley, 144, 347
Stathis, 149
Staudinger, 275, 276, 283, 284, 286, 387
Steacie, 134
Stein, 24
Steiner, 309, 324
Stepp, 112
Stern, 296
Stevinson, 232
Stickhorn, 233
Stieglitz, 240
Stirton, 294
Stone, 243
Storch, 339, 351, 353, 354, 359, 360
Strauss, 19
Strecher, 262
Strutt, 308
Stuer, 324
Suen, 417
Sullivan, 14, 77, 78
Svedberg, 166
Swann, 183, 237
Sweeney, 362, 366, 368
Szabo, 241

Tanz, 144
Taube, 262

Taylor, G. B., 191
Taylor, H. S., 8, 33, 36, 39, 42, 51, 82, 87, 88, 109, 111, 127, 130, 183, 207, 212, 218, 221, 234, 309, 320, 339, 342
Technical Research Works Limited, 401
Teller, 32, 109, 182
Temkin, 310
Terry, 263
Testrup, 401
Texas Company, 378
The Selden Company, 203
Thenard, 6
Thiele, 323, 384
Thiessen, 133
Thomas, 109, 116, 138, 149, 252, 374
Thornhill, 139
Thorp, 195
Tilden, 384
Tilley, 163, 191, 319
Tinker, 218
Todd, 362
Tokunaga, 404
Tollens, 7, 243
Tommila, 239
Traube, 187
Trautz, 324
Trickey, 272, 273
Tropsch, 128, 170, 199, 266, 329, 330, 336, 340
Tsellinskya, 183
Turkevich, 212
Twigg, 32
Twitchell, 420, 421
Twyman, 19

Ubbelohde, 197
Uehara, 191
Ueno, 402, 404
Ufer, 415
Uhde, 314
Underwood, 336, 338
United States Industrial Chemicals, Inc., 391, 392, 393, 394
United States Rubber Co., 395
United States Tariff Commission, 304
Universal Oil Products Company, 372, 376

Vail, 423
Vainshtein, 318
Van Arsdel, 403
Van Duze, 229
van Oordt, 307, 310
Varga, 354
Vaughan, 100, 145, 252
Veil, 113
Verbeck, 321
Verein chemischer Fabriken, Hasenbach and Clemm, 7
Verheus, 213
Vernon, 178, 249
Vidyarthi, 263
Vlodrop, 263, 403
Vogel, 326, 385
Vogt, 235
Voog, 206
Vorhees, 52, 53, 166
Vorhies, 362

Waals, van der, 75
Wachter, 282
Wagner, 89, 359
Waldschmidt-Lietz, 183
Walker, 204
Walta, 66
Walter, 273
Walters, 148
Warren, 93, 94, 358
Washburn, 21
Wassermann, 182
Waterman, 145, 403
Watson, 191
Watt, 295
Webb, 318
Webster, 148
Wehrli, 275
Weinmayer, 218
Weinrich, 256
Weiss, 203, 204
Weissberger, 41
Weiz, 189
Wells, 402
Welsh, 405
Weltzenbock, 217
Werner, 266
Wheeler, 33, 58, 101, 199
Whitby, 275, 285, 384, 386, 390
Whitehead, 163
Whitney, 89, 291
Wieland, 185
Wiesevich, 200, 340
Wiggins, Henry, & Co., 152

Wiley, 21
Willforth, 204
Williams, 19, 129, 206, 252, 280, 347, 384, 386
Willstätter, 111, 183, 198, 299
Wilson, 80
Winans, 224, 227, 231, 232
Winkler, 7
Wohl, 8, 291
Wojick, 227, 289
Wolff, 135, 289
Wolski, 16
Wood, 148
Woodhouse, 243, 248
Woodruff, 315
Woodward, 252
Woodworth, 339
Wooj, 206
Work, 359
Wulff, 256
Wurster, 155, 397
Wurster & Sanger, Inc., 156, 399, 400
Wyckoff, 30

Yanasheva, 158
Young, 129, 299

Zamomoto, 140
Zartman, 223, 230
Zelinsky, 227
Zenghelis, 149
Ziegler, 129, 269
Zinke, 269
Zobel, 183
Zsigmondy, 133
Zuiderweg, 213

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Borrower's No.	Issue Date	Borrower's No.	Issue Date

SUBJECT INDEX

Acenaphthene, dehydrogenation of, 207
Acenaphthylene from acenaphthene, 207
Acetaldehyde condensation, 325
  decomposition of, 67
  from acetylene, 8, 235, 324
  from ethyl alcohol, 207
  from ethylene oxide, 265
  oxidation of, 298
Acetals, hydrogenolysis of, 229
Acetic acid, anhydrous, promoter action of, 287
  acid, dehydration to acetic anhydride, 244
  acid, dehydration to ketene, 244
  acid, from acetaldehyde, 298, 325
  acids, salt effect, 74
  anhydride, impurities in, 13
  anhydride production, 244
Acetoacetic ester, catalysis of keto-enol change, 78
Acetone, formation of, 268
  from calcium carbide, 324
  from isopropyl alcohol, 210
Acetyl fluoride, formation of, 250
Acetylene, as catalyst poison, 319
  as source of Buna rubbers, 388
  compounds, ring closures, 217
  condensation products from, 328
  condensation with phenols, 135
  derivatives, production of, 324
  hydration in vapor phase, 327
  hydration of, 235
  hydrogenation of, 222
  intermediary compounds with mercury salts, 327
  phenol from, 329
  polymerization of, 386
Acid and base, definition of, 71
  as depolymerization catalyst, 286
  strong, as catalyst, 247
  sulfates, 145
Acid-base catalysis, 70
  catalysis, kinetics of, 72
Acidolysis, 245, 247
Acrolein formation, 243
Acrolein from allyl alcohol, 210
Acrylonitrile (vinyl cyanide), 394
Activated adsorption, 87
  adsorption of oxygen on silver, 89
  carbon for removal of hydrogen sulfide, 312
  carbon, oxidation of nitric oxide, 306
  charcoal as chlorination catalyst, 340
  charcoal, hydration catalyst, 235
  clays, 179
  hydrosilicate of alumina, motor fuels, 375
  montmorillonite, 180
Activation energy, 103
  energy, activated adsorption, 88
  energy, aromatization, 217
  energy, o-benzoylbenzoic acid, 266
  energy, chain reactions, 41, 42
  energy, hydrolysis phthalic acid esters, 240
  of nickel by anodic oxidation, 402
  of nickel catalysts, 159
  of oxidation catalysts, 175
  of oxygen, 185
Activator, nickel catalyst, 160
Active centers, 34
  in chain reactions, 44
  iron catalysts, 311
Active group, in organic catalysts, 300
Activity, acid-base catalysis, 70
  activated alumina, 137
  alkylating acid, reduction of, 379
  alloys, 170
  aluminum chloride, 253
  catalysts, 83
  catalytic contact surface, 92
  chromium oxide, 145
  coal hydrogenation catalysts, 93
  cobalt catalysts, 151
  crystal structure, 234
  eight group elements, 118

Activity (*Cont.*):
  enzyme reactions, 300
  gauze temperatures, 165
  halide catalysts for alkylation, 257
  hydrogenation catalysts, 220
  hydroxides and oxides in fat hydrolysis, 419
  iron catalysts, 311
  Kogasin catalysts, 336
  methyl alcohol catalysts, 342
  nickel catalysts, 92
  nickel formate catalysts, 157
  organic catalysts, 300
  particle size, 133
  platinum-rhodium catalysts, 163
  radioactive method, 95
  zinc oxide, 134
Addition, CO to ether or alcohol, 248
  ethylene to acids, 245
  hydrogen fluoride to double and triple bonds, 250
  in esterification, 245
  isobutylene to phosphoric acid, 254
Adsorption, 83
  activated, 83, 87
  chemisorption, 83
  gases on impure metals, 51
  hydrogen, 88
  hydrogen on iron, 89
  hydrogen on K_2O, 310
  isotherms, 84
  nitrogen on K_2O, 310
Aerogels, 179
Affinity of enzymes for substrate, 296
Agitation plants for oil hydrogenation, 398
Air as polymerization catalyst, 284
Alanin as catalyst, 301
Alcohol, addition of CO, 248
  dehydration of, mechanism, 242
  formation, catalyst for, 343
  oxidation of acetaldehyde, 385
Alcoholic fermentation, 299
  potash as polymerizing agent, 384
Alcohols, decomposition on bauxite, 105
  dehydrogenation, 136
  dehydrogenation and dehydration, surface mechanism, 99
  from esters, 233
  from Fischer-Tropsch synthesis, 344
  from glycerides, 411
Alcohols (*Cont.*):
  from olefins, equilibrium, 236
  higher, and esters by hydrogenation of oils, 410
  high-molecular, sulfonation in presence of aldehydes, 287
  hydrogen donors in hydrogenation, 409
  hydrogenation from oleic acid, 411
  oxidation mechanism, 202
  production of, 340
Alcoholysis, 245, 247
  fat splitting by, 423
Aldehydes and ketones from alcohols, 205
Aldehydes as hydration catalysts, 236
  hydrogenation of, 208
Aldol, 326
  condensations, 269
  from ethylene, 394
Aldol-naphthyl amine as inhibitor, 52
Alkali amides, molten, for gas purification, 314
  carbonates, 322
  cyanide formation, 322
  halides as wall catalysts, 109
  promoter action in Kogasin catalysts, 335
Alkalies, 129
  true volumes, 122
Alkaline earth-metal catalysts, alcohol formation, 345
  earths, 129
Alkene linkage, 221
Alkyd resins, 272
Alkyl chlorides, 337
  naphthalene sulfonic acid (Nekal), 420
  substituted paraffins, formation, 253
  sulfate, 253
  sulfates, formation of, 378
Alkylation, 252
  auto-destructive, 258
  benzene and olefins, 253
  chloride catalysts, 253
  dealkylation, 252
  definition, 255
  destructive, 258
  halide catalysts, 257
  higher paraffins, 255
  hydrocarbons, aromatic, 252

Alkylation (*Cont.*):
  hydrocarbons, motor fuel, 377
  hydrogen fluoride catalyst, 258
  isobutylene and benzene, 254
  isoparaffinic compounds, 260, 261
  metal alkyls, 252
  naphthalene, 255
  naphthenes, 255
  phenols, 254
  product, 381
  utilization of lower paraffins, 377
Alkyls of metals, 252
Allotropic change of cobalt, 123
  of iron, 123
  of nickel, 123
  of tin, 123
  changes in metals, 122
  forms of iron, 82
  forms of nickel, 82
Alloy (binary) catalysts, water formation, 118
  catalysts, 335
Alloys, activity of, 170
  catalysts from, 129, 130
  platinum-rhodium, 163
  with nickel: Al, Si, Na, Ca, Mg, 158
Allyl alcohol, 222
  alcohol, dehydrogenation of, 210
Almond oil, exhaustively hydrogenated, 397
Alumina, 243
  activated, for dehydrogenation, 207, 338
  active, 136
  as carrier, 177, 215
  as catalyst, 242
  as condensation catalyst, 268
  as dehydration catalyst, 242
  as dehydrogenation catalyst, 205
  catalyst promoted with nickel, 241
  chromia reforming catalysts, 375
  dehydration of acetaldehyde, 385
  dehydration of alcohols and ammonia or amines, 292
  gel ammonium molybdate catalyst, 359
  gel, oxidation of nitric oxide, 306
  isomerization catalyst, 264, 265
  quartz catalyst, 321
  silica catalyst, motor fuels, 375
Aluminum, 322
Aluminum (*Cont.*):
  amalgam as bromination catalyst, 250
  chloride, 136, 338
  chloride, activity of, 253
  chloride, anhydrous, impurities in, 13
  chloride as alkylation catalyst, 255
  chloride as chlorination catalyst, 328
  chloride as dechlorination catalyst, 250
  chloride as decomposition catalyst, 257
  chloride, isomerization, 374
  chloride, ring closure catalyst, 217
  crystallized trihydrate of, 136
  ethoxide, 325
  ethylate, 325
  halides, 138
  iron chloride catalyst, 253
  phosphate catalyst, 243
  sulfate, 243
  sulfate as dehydration catalyst, 243, 244
Alums, dehydration of castor oil, 416
Alundum carrier, 178
Alvars, 326
Amalgams for making catalyst surfaces, 172
American ammonia process, 315
American coals, hydrogenation of, 354
Amides, acid, by ammonolysis, 294
  dehydration of, 243
  hydrogenolysis of, 233
Amination, 291
  amines by hydrogenation, 293
  aniline from nitrobenzene, 291
  glucamines from monosaccharides, 294
  iron catalyst, 292
Amines, aromatic, alkylation of, 253
  from alcohol and ammonia, 292
  from amides, 233
  in petroleum feeds, 379, 380
  primary and secondary, from cyanides, 223
  secondary, preparation of, 230
Amino alcohols, hydrogenation of, 231
β-Amino amides, hydrogenation of, 231
β-Aminobutyric acid as catalyst, 300

α-Aminocyanides, hydrogenation of, 231
α-Amino-isobutyric acid, 301
3-Amino-α-napthoxindol, as catalyst, 301, 303
3-Amino-oxindole, as catalyst, 301
3-Amino-oxindol-6-carbonic acid, as catalyst, 302
3-Amino-6-oxy-α-napthoxindol, as catalyst, 303
3-Amino-7-oxy-α-napthoxindol, as catalyst, 303
3-Amino-8-oxy-α-napthoxindol, as catalyst, 303
Ammonia as catalyst, 247
  catalysis, nitride theory, 102
  catalysts, 150
  catalysts, poisons, 311
  high-pressure synthesis of, 7
  manufacture of, 311
  oxidation, 316
  oxidation, catalyst for, 164
  oxidation, mechanism, 317
  oxidation of, 190
  production, world capacity, 315
  synthesis, activity of iron catalysts, 30
  synthesis, equilibrium concentrations, 307, 308
  synthesis, kinetics of, 310
  synthesis of, 307
  synthesis, partial reactions of, 102, 103
  synthesis, scheme, 309
Ammonium carbonate as precipitant, 153
  carbonate, formation of, 221
  chloride as ammanolysis catalyst, 295
  chloride-stannous sulfide catalyst, 359
  chromate, 145
  metavanadate, 144
  molybdate, 304
  nitrite, formation of, 187
  salt as ammonolysis catalyst, 294
  sulfate, formation of, 321
  vanadate, 143
Ammonolysis, 294
  ammonium chloride as catalyst, 295
  ammonium salts, 294
  chlorobenzene, 294
Ammonolysis (*Cont.*):
  copper salt, mixed, 294
  cuprous oxide, 294
  glycerides of long-chain fatty acids, 295
Amphotere nature of enzymes, 296
  properties, solvents, 72
Amyl alcohol by Fischer-Tropsch synthesis, 336
  benzenes, 253, 254
Analytical range of substances, 11
Aniline as catalyst, 301
  by reduction of nitrobenzene, 141
  from azobenzene, 233
  from chlorobenzene, 8, 175, 291, 294
Animal oils and fats, technical hydrogenation, 397, 398
Anion acids, 71
Anisole as negative catalyst, 36
Antagonism, biochemical, 111
Anthracene, destructive hydrogenation, 362
  hydrogenation of, 225
  oxidation of, 204
Anthraquinone from anthrocene, 204
  from o-benzoylbenzoic acid, 266
  sulfonation of, 286
Anthroxylon, hydrogenation of, 355
Anti-enzymes, 296
Antiknock compounds, 36
  value of octanes, 373
Antiknocks, colloidal metals, 108
  iron pentacarbonyl, 108
  tetraethyl lead, 108
Antimony catalyst, water formation, 104
  flouride as fluorine carrier, 250
  pentachloride, 142, 328
  trichloride, 142
Anti-oxidants, 52
  for rubber, 36
Apparatus lined with catalyst, 132
Aromatic compounds, oxidation of, 202
  derivatives, synthetic rubber from, 393
  hydrocarbons, alkylation, 252
  hydrocarbons, destructive hydrogenation, 349
  sulfonic acids as catalysts, 247, 249
Aromatics, side chains in cracking, 349

Arrhenius' equation, modified, 103
Arsenic, 142
  poison for ammonia catalysts, 311
Arsine as catalyst poison, 319
Asbestos, 308
  flour, 335
  support for nickel catalyst, 160
Ascorbic acid, autoxidation of, 40
Ashes of coal, catalytic activity of, 358
Aspergillus niger, growth substance for, 14
Association mechanism in exchange reaction, 100
Atomic carbon, 101
  field forces, overlapping, 111
  hydrogen, 107, 308
  nitrogen, 308
Atoms, freedom of motion, 262
  of chlorine, 251
Attrital matter, hydrogenation of, 355
Autocatalysis, 38
  of amphotere compounds, 41
  nature of in acid-base catalysis, 41
Autocatalytic path, polymerization, 275
Autoclave process, hydrolysis of fats and oils, 419
Auto-destructive alkylation, 258
Autolysis of enzymes, 295
Autoxidation, 185
  of ascorbic acid, 40
  of β-eleosteric acid, 40
  of linseed oil by air, 39
  of sulfite solutions, 189
  rate of, 37, 39
Aviation gasoline, 361
  gasoline catalyst for, 180
Azobenzene, hydrogenation of, 233

Bakelite, 269
Barium cyanide formation, 323
Base-exchange catalysts, 246
Base metal catalysts from amalgams, 135
Bases as depolymerization catalysts, 286
Bauxite catalyst for decomposition of alcohols, 105
  catalyst impregnated with $AlCl_3$, 181
Benzaldazine, hydrogenation of, 233
Benzaldehyde from benzyl alcohol, 210
  from toluene, 203
  hydrogenation of, 223
Benzene, alkylation with ethylene, 253
  alkylation with propylene, 253
  chlorination, 250
  condensation with olefins, 253
  from cyclohexane, 205
  from n-hexanes and n-hexenes, 217
  hydrogenation of, 224
  hydrogenation with various catalysts, 234
  in presence of HF, 259
  oxidation of, 203
  stearosulfonic acid, 420
  sulfonation, 287
Benzenes, amyl, 253, 254
  substituted, 253
Benzenoid nucleus, hydrogenation of, 224
Benzine from water gas, 332
  from water gas, tabulation of, 334
Benzoic acid esters, alkaline hydrolysis of, 240
  acid, from toluene, 203
  acid, sulfonation, 287
Benzotrichloride, 250
Benzotrifluoride, 250
o-Benzoyl benzoic acid, condensation to anthraquinone, 266, 267
Benzoyl carbinol, hydrolysis catalyst, 238
  peroxide, 251
Benzyl alcohol, dehydrogenation of, 210
  alcohol from benzaldehyde, 223
  alcohol, hydrogenolysis of, 228
  amine and dibenzyl amine from benzaldazine, 233
  cyanide, 244
  dioxytriazine by desulfurization, 288
  dioxytriazine toluene, 288
  methyl ether from benzyl and methyl alcohols, 243
  sulfide, desulfurization, 289
  sulfoxy triazine ether, 289
Beryllium chloride, 257
Biological systems, catalysis in, 14
Bismuth oxide, 142
  salts, hydration, 344
Bituminous coal, high-volatile, hydrogenation of, 355

Bituminous (*Cont.*):
  coal, hydrogenation of, 357
Blast furnace gas, 332
Bonding strength and structure, 350
Bone black as chlorine carrier, 250
Boric acid, 136
Borneol, dehydrogenation of, 206
  hydrogenation of, 49
Boron fluoride, 257
  halides, 136
  phosphate, 424
Brass, best dehydrogenation catalyst, 208
Bridges in resins, 273, 274
Bromides of Fe^{III} and Al as iodine carriers, 250
Bromine, 148, 304
  carriers, 250
  inhibiting action of, 65
5-Bromo-3-amino-oxindol as catalyst, 302
Bromosuccinic acid, rate of hydrolytic decomposition, 37
Buna 85, 387
Buna rubbers from acetylene, 388
Buna S, 387, 393, 394
Buna S rubber, production of, 395
Buna SS, 391
Butadiene, 384
  acrylic nitrile polymer, 387
  from ethyl alcohol, 385
  polymerization, 384, 387
  potential U. S. supply, 388
  raw materials for, 388
  styrene polymer (Buna S), 387
1,3-Butadiene from n-butenes, 206
Butene, polymerization of, 373
Butene-1-ol-3, dehydrogenation of, 208
Butvars, 326
Butyl acetate from ketene, 248
  alcohol, dehydrogenation of, 207
  alcohol, formation of, 175, 326
  alcohol from butylene, 235, 344
  alcohol from ethyl alcohol, 345
  alcohol from lower alcohols, 345
  aldehyde, formation of, 326
  aldehyde from butyl alcohol, 207
  mercaptan, desulfurization of, 289
  rubber, 392
n-Butyl cyanide, 244
Butylene glycol monoacetate, 326
  hydration of, 235
Butylene (*Cont.*):
  polymerization, 282, 367
1,3-Butylene glycol from ethylene, 394
Butyranilide from 1-phenyl-3-methylpyrazolone-5, 233
Butyric acid methyl ester, 238

Cadmium, 135
  metaphosphate, 135
  sulfide, desulfurization catalyst, 288
Calcium carbide, synthetic rubbers derived from, 392
  chloride, 322
  chloride or oxide, 412
Camphor, hydrogenation of, 49
  production of, 206
Cane sugar, inversion of, 73
Carbides, intermediary formation in Kogasin synthesis, 334
Carbohydrases, 207
Carbohydrates, hydrolysis by enzymes, 297
  polyalcohols from, 347
Carbon, activated, 139
  atomic, 101
  deposit on contact mass, 137
  deposit on cracking catalyst, 366
  deposit on nickel catalyst, 225
  derivatives, polymerization tendency, 278
  dioxide, chemisorption of, 31
  dioxide for Kogasin synthesis, 333
  dioxide, formate from, 223
  dioxide, reduction of, 169
  dioxide, removal from gas mixture, 312
  disulfide, 406
  disulfide as negative catalyst, 36
  disulfide, desulfurization of, 288
  hydride, 59
  impregnated, 423
  monoxide, addition to ether or alcohol, 248
  monoxide, chemisorption of, 31
  monoxide, conversion to methyl alcohol, 341
  monoxide, dry combustion of, 63
  monoxide, hydrogenation of, 98, 329
  monoxide, mechanism of oxidation, 29
  monoxide, nickel poison, 369, 406

Carbon (*Cont.*):
  monoxide, poison for ammonia catalysts, 311
  monoxide, preferential formation, 342
  monoxide reduction over copper contacts, 334
  monoxide removal from air, 172
  monoxide, steam and olefins, acids from, 423
  monoxide, wet combustion of, 63
  oxides and water gas, products from, 329
  platinized, 217
  tetrachloride, 340
  tetrachloride from methane, 251
  to carbon bonds, hydrogenation of, 229
  to metal bonds, hydrogenolysis of, 228
  to nitrogen bonds, hydrogenation of, 230
Carbonyls, hydrogenation of, 222
Carboxylase models, systematic substitution of, 300
Carboxylases, 299
Carboxylic acids, formation of, 423
Carrara silicate, 144
Carrier substance for vanadium-platinum catalyst, 144
Carriers, 173
  for nickel catalysts, 160
  function of, 335
  of high-polymers, 179
Casale ammonia process, 313
Castor oil acids (hydrogenated) naphthalene sulfonic acids (Pfeilring), 420
  oil dehydration of, 412
  oil exhaustively hydrogenated, 397
  oil molecular weight of, 414
  oil natural and dehydrated, properties, 413
Catalase, 299
Catalases, molecular weight, 296
Catalysis, definition of, 1
  general mechanism of, 4
  in intramolecular change, 77
  in mixtures, 111
  in solids, 109
  mechanism, water gas conversion, 331
Catalyst, Adam's, 224
  alumina, 242
  bed, 375
  chromium trioxide, 198
  cobalt, 194
  copper stearate, 195
  definition of, 1
  elements, 401
  hydrogenation, specifications of, 219
  life, 336
  linoleates, 196
  methylalcohol formation, 176
  nickel, 194
  oleates, 194
  orthophosphoric acid, 242
  osmium tetroxide, 198
  oxidized paraffin, 196
  palmitates, 196
  poison as promoter, 56
  poisons as promoters, mechanism of, 18
  poisons, electron octet theory, 57
  poisons in oil and fat hydrogenation, 406
  poisons in vegetable and animal oils and fats, 402
  poisons, typical, 54
  resinates, 196
  tablets, 147
  Thermofor Catalytic Cracking Synthetic Bead, 180
  thoria, 242
  vanadium pentoxide, 198
  zinc chloride, 242
Catalysts, dehydrogenation, 204, 205
  esterification, 246
  finely divided, 366
  for alcohol formation, 343
  for dehydration of castor oil, 414
  for generating hydrogen from hydrocarbons, 128
  for hydrogenation of oils and fats, 408
  for Kogasin synthesis, 334
  for oxidation of CH_3OH, vanadium oxide, 202
  for reduction of SO_2, preparation of, 138
  for ring closures, 217
  for sulfonations, 286
  from silicon alloys, 335
  Hopcalite, 172

Catalysts (*Cont.*):
  iron-alumina, 150
  iron oxide, preparation of, 150
  mixed, 170
  platinum, 162
  polymerization, 278, 279
  positive, 10
  precipitated, 335
  p-toluene sulfonic acid, 416
Catalytic action of mineral waters, 187
  change, isomerization in, 265
  coefficient, 80
Catalytically active substances, defintion, 115, 116
Cathodic dispersion, 167
Cation acids, 71
Cellulose acetate, catalysts in formation of, 249
Cellulose hydrolysis, 238
Ceria catalyst, 321
Cerium compounds as oxidation catalysts, 188
  oxide, 138
Cesium vapor, adsorption on tungsten, 85
Chain branching, 43
  length, branching chain, 45
  length, determining factors, 65
  length, non-branching, 43
  reaction, autoxidation of sodium sulfite, 189
  reaction, breaking of in negative catalysis, 37
  reaction, decomposition of H_2O_2, 187, 190
  reaction, mechanism, 42
  reaction, oxidation of aldehydes to acids, 198
  reaction, oxidation of hydrocarbons, 195
  reactions, 41
  reactions, criteria for, 42
  reactions, heterogeneous, 106
  reactions in combustion of motor fuel, 108
  reactions, in homogeneous catalysis, 63
  reactions induced by alkali vapor, 64
  reactions, material or chemical chains, 41
Chain (*Cont.*):
  reactions, physical or energy chains, 41
  reactions, velocities, 45
Charcoal, activated, 248
  activated, impregnated, 235
  as chlorine carrier, 250
  catalyst, p-o-hydrogen conversion, 107
  impregnated, 423
Chart, temperature record of reduction of nickel formate, 157
Chemical action of minor constituents of zinc, 17
  composition (purity), 10
  elements and compounds in catalysis, 123
    Group I, 129
    Group II, 133
    Group III, 135
    Group IV, 139
    Group V, 141
    Group VI, 144
    Group VII, 148
    Group VIII, 149
  reactivity of substance, 16
Chemicals from natural gas, 339
Chemigum, 392, 394
Chemisorption, ethylene on nickel catalyst, 100
  of nitrogen on tungsten, 102
Chlorides as chlorine carriers, 250
  metallic, cyanamide and cyanide catalysts, 322
  of Al and Fe^{III} as iodine carriers, 250
  of Al, Fe^{III}, and Hg as bromine carriers, 250
Chlorinated compounds from acetylene, 327
  hydrocarbons, dechlorination of, 250
Chlorination catalysts, 340
  exhaustive, 328
  of benzene, 250
  of Kogasin II, 337
  of methane, 251
  of natural gas, 340
  of toluene, 250
  of xylenes, 250
Chlorine, 148, 304
  as catalyst poison, 58
  carriers, 250

Chlorine (*Cont.*):
  production of, 7
Chlorobenzene, ammonolysis of, 294
2-Chloro-1,3-butadiene, 386
Chloroform as negative catalyst, 36
Chlorophyll, 2
Chloroprene, development of, 386
  preparation of, 386
Chlorosulfonic acid, 287
Chromia catalyst, dehydrogenation-condensation, 211
Chromia-alumina catalyst, dehydrogenation, 137
Chromite catalysts, 146
Chromium, 323
  active and inactive acids, 113
  amine catalysts, 80
  oxide, 145, 147
  oxide, adsorption of nitrogen on, 32
  oxide catalyst for cyclization, 212, 213
  oxide on active alumina, 177
  oxide on alumina, 375
  oxide on alumina containing a little water, 376
  sesquioxide, 342
  trioxide, 198
Cinnamic acid, formation of, 266
  acid, hydrogenation in solvents, 77
Cis-type fatty acids, 405
Citric acid, 272
Claude ammonia process, 313
Clay, porous burned, support for nickel catalyst, 160
Clays, activated, 179
  dehydration of castor oil, 415
Coagulation, slow, rate of, 40
Coal hydrogenation, factors involved, 352
  hydrogenation of, 348
  kinetics of hydrogenation, 351
Coals, American, hydrogenation of, 354
Cobalt, 151, 310
  acetate, 327
  activated with zinc oxide, 331
  allotropic change, 123
  catalysts, activity of, 151
  catalysts, mixed, 335
  contact, copper-promoted, 336
  molybdate, desulfurization catalyst, 291
Cobalt (*Cont.*):
  oxide in oxidation catalysts, 173
  oxide, reduction of, 151
  paint-driers, 152
  stearate as oxidation catalyst, 195
  subsulfide, preparation of, 291
  -amine catalysts, 80
  -magnesium catalysts, 151
  -thoria catalysts, 151
Coenzymes, 51, 296
Coke, impregnated, chlorination catalyst, 340
  oven gas, desulfurization of, 288
Collidine, 218
Colloidal metals, 166
  palladium, 169
  platinum, 164
  uranium oxide, 148
Coloring of fatty acids, 417, 418, 420
Combined dehydrogenation-polymerization-hydrogenation, 376
Combustion engine, reaction in cylinder, 107
Composition of acid sulfates, 145
  alkali metals, 129
  alkaline earths, 133
  alumina, 136
  aluminum, 135
  aluminum chloride, 138
  antimony, 141
  barium, 133
  boron, 135
  bromine, 148
  cadmium, 133
  calcium, 138
  carbon, 139
  chlorine, 148
  cobalt, 149
  copper, 129
  germanium, 139
  gold, 129
  hydrogen, 123
  indium, 135
  iron, 149
  lead, 139
  lead carbonate, 141
  lead nitrate, 141
  lead sulfide, 141
  lithium, 129
  magnesium, 133
  matter, gradation of, 15
  mercury, 133

Composition (*Cont.*):
  nickel, 149
  nickel sulfate, 152
  nitrogen, 141
  osmium, 150
  phosphoric acid, 141
  potassium, 129
  rhenium, 148
  rubidium, 129
  ruthenium, 150
  silicon, 139
  silver, 129
  strontium, 133
  sulfuric acid, 145
  tin, 139
  titania, 141
  zinc, 133
  zinc chloride, 134
  zinc oxide, 139
  zirconia, 141
  zirconium, 139
Composition (purity), 113
Compound formation, solvent and solute, 75
Condensation, 266
  acetaldehyde to ethylacetate, 325
  aceytlene with phenols, 135
  aldol, 269
  alkaline and acid catalysts, 270
  alkyd resins (glyptals), 272, 273
  alumina catalyst, 268
  anthraquinone synthesis, 267
  benzaldehyde and malonic acid, 266
  o-benzoyl benzoic acid, 266
  bridges, 273, 274
  cinnamic acid, formation of, 266
  coumarone-indene resins, 274
  cross linkages, 272
  ethyl alcohol, 267
  isomers, 272
  ketones and phenol, 269
  lubricating oils from water gas, 266
  nitroparaffins, 268
  olefinic hydrocarbons, 266
  phenols and aldehydes, 269
  products from acetylene, 328
  unsaturated methyl ketone synthesis, 267
  urea-formaldehyde, 273
Conjoint polymers. See copolymers.
Conjugation assays of vegetable oils, 263, 264
Conjunct polymerization, 280
Consecutive reactions, 98
Contact action, 5
  mass, 115
  mass, influence of carrier, 177
  period, oxidation of ammonia, 317
  process for oxidation of SO_2, 191
  surface, evolution of heat on, 18
  surface, examination of, 92
Continuous hydrogenation plant for oil hydrogenation, 401
  hydrogenation, quality of product, 406
Converter for laboratory control, 94, 95, 96, 97
Converters, cylindrical, 398
Copolymers (conjoint polymers), 284
Copper, 129, 322
  as dehydrogenation catalyst, 207
  catalyst activated with nickel, poisoning of, 56
  catalyst, adsorption of nitrogen on, 32
  catalyst, esters and alcohols from oils, 410
  catalyst, hydrolysis, 241
  catalyst, methyl alcohol-water reaction, 106
  catalyst, mixed, 209
  catalyst, water formation, 104
  catalysts, 129, 342
  catalysts, from organic salts, 132
  catalytic action in ammonia solutions, 187
  chloride catalyst for oxidation of phosphorus, 193
  chromate, basic, esters and alcohols from oils, 411
  chromite, 227, 233
  chromite, esters and alcohols from oils, 411
  chromite, selectivity, 96, 98
  chromium oxide, 221, 222
  chromium oxide catalyst, 131
  chromium oxide, preparation of, 145
  cobalt catalyst, 347
  contacts, reduction of CO, 334
  decomposition of methyl alcohol, 342
  gauze catalyst, 385
  in autoxidation of ascorbic acid, 40, 41

Copper (*Cont.*):
  nickel catalyst, 347
  oxide, 304
  oxide, reduction of, 130, 134
  oxide with 10% UO_3 as catalyst, 248
  promoted cobalt contact, 336
  promoter action in Kogasin catalysts, 335
  reduced, and zinc oxide (methyl alcohol catalysts), 294
  salt, mixed, as ammonolysis catalyst, 294
  stearate as oxidation catalyst, 195
  technical, spectrographic analysis of, 13
  tube for dehydrogenation, 210
  vanadyl zeolite, 175
  wire, treated as catalyst, 130
  zinc catalysts, preparation of, 134
  zinc catalysts, X-rays of, 134
  zinc oxide catalysts, 132
Cottonseed oil, hydrogenation of, 404
Cottonseed oil, shortening from, 405
Countercurrent system, 371
Coupling in acid alkylation of hydrocarbons, 378
Cracking, 374
  catalyst, deposit of carbon on, 366
  West Texas crude, 365
Criteria for chain reactions, 42
Critical explosion limit, 66
  reaction complex, 36
Cross linkages, 272
Croton aldehyde, 326
  aldehyde reduction, 175
Crotonic acid, formation of, 326
  acid, influence of poisons, 57
Crushing load, carrier strength, 180
Crystal growth, prevention of, by promoter, 51
  planes and activity, 33, 101
  structure and activity, 234
  surface forces of, 34
Cupric chloride on pumice, chlorination, 251
Cupric/cuprous oxide-copper mechanism in oxidation, 187
Cuprous chloride with ammonium chloride, polymerization, 386
Cyanamide, catalyst for production, 7
Cyanide, hydrogen, from acetylene and ammonia, 321
  hydrogen, from CO and NH_3, 321, 322
  hydrogen, from formamide, 322
Cyanides as catalysts, 343
  from amides, 243
  from organic acids or esters and ammonia, 243
  hydrogenation of, 223
Cyanogen and nitric oxide, reaction between, 69
  as catalyst, 69
Cyclization acetylene compounds, 217
  and other ring closures, 212
  catalysts for, 215
  chromium oxide catalyst, 212, 213
  dehydrocyclization, 215
  α-dinaphthyl, 217
  ethylene compounds, 218
  n-heptane, of, 212, 215, 217
  n-hexanes and hexenes, 217
  hydrocarbons, aliphatic, mechanism, 213
  hydrocarbons, aliphatic, structure, 214
  hydrogen fluoride catalyst, 218
  isobutane, 217
  n-octanes, 217
  rate of, 217
1,3-Cyclohexadiene, 20
Cyclohexane, 224, 393
  absorption curve of, 20
  dehydrogenation on platinum, 120
  from benzene, 205
Cymene stearo sulfonic acid, 420
p-Cymene, 20

Dalton's atom theory, 4
Dealkylation of ethylbenzene, 252
Deammonation, 219
Decarbonation, 219
Decarboxylation of trinitrobenzoic acid, 76
Dechlorination of chlorinated hydrocarbons, 250
Decomposition of acetaldehyde, 67
  of alcohols on bauxite, 105
  of ammonia, heats of activation, 103
  of ammonium nitrate, 304
  of ethers, 68
  of ethers, heat of activation, 105

Decomposition (*Cont.*):
  of ethylene, chain mechanism of, 66
  of hexane, 257
  of high-molecular-weight hydrocarbons, 257
  of hydrocarbons, 257
  of hydrogen peroxide, 6
  of hydrogen peroxide by gold sols, 133
  of hydrogen peroxide in presence of iron citrate, 48
  of intermediary compounds, 200, 201
  of methyl alcohol, 107, 342
  of nitrogen peroxide, 307
  of nitrous oxide, 304
  of oxygen and hydrogen, 119
  of temperature, specific, 349
  of xanthic acid, 76
Dehalogenation, 219
Dehydrating oxides, 49
Dehydration, 242
  of alcohol and ammonia mixture, 292
  of alcohols, 99, 209
  of castor oil, 412
  of castor oil, mechanism of, 416
  of formamide, 322
  intramolecular, 345
Dehydrocyclization, 215
  of aliphatic alcohols, 211
Dehydrogenases, 298
Dehydrogenation, 185, 204
  acenaphthene, 207
  alcohols, 99, 136
  allyl alcohol, 210
  benzyl alcohol, 210
  borneol, 206
  brass catalyst, 208, 210
  butene-1-ol-3, 208
  n-butenes, 206
  butyl alcohol, 207, 209
  catalysts, 137, 205, 206, 207
  chrome-alumina catalyst, 137
  cyclohexane, 205
  cyclohexane on platinum, 120
  ethyl alcohol, 207, 209
  ethyl benzene, 207
  hydrocarbons, 136
  hydrocarbons and olefins, 205
  isoborneol, 206
  isobutene, 208
Dehydrogenation (*Cont.*):
  isopropyl alcohol, 210
  methyl isobutyl carbinol, 210
  mono olefins to diolefins, 206
  oxidation mechanism, in, 197, 198 202
  oxide catalysts, 209
  paraffins, 375
  pentenes, 206
  primary and secondary alcohols, 208
  propyl alcohol, 209
  rhenium catalyst, 209
  secondary alcohols, 210
Deodorized fat, 396
Depolarizing action of minor constituents, 17
Depolymerization, 285
Deposition of carbon on cracking catalyst, 366
  of catalysts on active carbon, 139
  of catalysts on carriers, 176
  of platinum on surfaces, 168
Desal, 41
Desorption, 89
  enzyme reactions, 296
  heat of, 103
  in aromatization, 212
  mechanism, 90
  retardation of, 36
Destructive alkylation, 258
  hydrogenation, motor fuels, 362
Desulfurization, 219, 288
  cobalt molybdate catalyst, 291
  of gasoline and gases, 291
  of organic sulfur compounds, 288, 289
  Raney nickel in, 288
Detergents, 412
Determinant, 16
Determination of rate of cyclization, 217
Detonation in gasoline engine, retardation or induction of, 37
Deuterated phosphoric acid catalyst, 282
Deuterium and olefins, exchange reaction, 100
α-Diamines, hydrogenation of, 230
Diatomaceous earth, 152, 322
Diatomite, support for platinum catalyst, 167
Diazoacetic esters, hydrolysis of, 241

Diazoaminobenzene, hydrogenation of, 233
Dibenzyl from stilbene, 222
5,7-dibromo-3-amino-oxindol as catalyst, 302
Dibutyl zinc, hydrogenolysis of, 228
Dichlorodifluoromethane, preparation of, 250
Dicyan, 236
Dienes, preparation and polymerization of, 384
Diesel fuels, 361
  oil, Kogasin II, 337
Diethyl benzene from ethyl benzene, 252
  ether, 340
  furfural acetal, hydrogenolysis, 229
  sulfate, 343
Diffusion of gases through metals, 83
  of hydrogen, 352
  through metals, nascent hydrogen, 124
Diisobutene, selective hydrogenation, 98
Diisopropyl ether, hydrolysis constant, 241
Diketene, production, 244
1,3-Diketones, hydrogenation of, 230
Dimer, acetaldehyde, 326
Dimethyl butadiene, 20
2,3-Dimethyl butadiene, 384
Dimethyl ether as catalyst, 340
  ether from methanol, 243
Dimethylolurea, formation of, 274
α-Dinaphthyl, ring closure, 217
Dioxanate catalysts, 246
Diphenyl magnesium, 228
  sulfoxide, 289
1,3-Diphenyl pyrazolone-5, hydrogenation of, 231
Dissolution of zinc, mechanism of, 17
  rate, 89
2,6-Di-tert-butyl-4-methyl phenol, preparation of, 256
Dithio ethylene glycol, 288
Divinyl acetylene, formation of, 386
Donors, hydrogen, alcohols as, 409
Double bond, position of, 213
  bonds, conjugated, 263, 413
  bonds, isolated, 413
Douglas fir wood tar, hydrogenation of, 360
Drugs, action of, 111
Dry distillation of vegetable oil soaps, 412
Drying oils and resins, absorption spectra of, 20
  oils, linkage shifts, 263
Durez, 269
Dust recovery equipment, 366

Elaidic-oleic acid change, 263
Elastothiomers, 392
Electric insulators from Kogasin wax, 336
Electrodeposition of catalytic metals, 172
Electron emission from heated tungsten wire, 29
  octet theory of catalyst poisoning, 57
  orbits, deformation of, 109
  process, oxidation of hydroquinone, 298
Electrostatic forces, 81
Elementary reactions, 61
α-Eleostearic acid, 20
β-Eleostearic acid, autoxidation of, 40
Emulsification of chloroprene, 386
Emulsifiers, 412
  formation of, 287
Emulsion, synthetic rubber, 395, 396
Energy of activation, 103
  of activation aromatization, 217
  or physical chain reactions, 41
Energy-rich molecule, 64
Enzymes (and organic catalysts), 295
  active group, 300
  activity, 300
  adsorption, 296
  amphotere nature, 296
  anti-enzymes, 296
  carboxylase, 299
  carboxylase models, 300
  catalase, 296, 299
  co-enzymes, 296
  dehydrogenases, 298
  desorption, 296
  electron process, 298
  esterases, 297
  heat lability, 296
  hydrogen peroxide, 300
  hydrolases, 297
  lipases, 297

Enzymes (*Cont.*):
  molecular weight, 296
  organic catalysts, 300
  oxidases, 299
  oxidation of acetaldehyde, 298
  oxidation-reduction, 298
  oxido-reductases, 298
  peroxidases, 299
  saccharase, 299
  selectivity, 295
Equilibrium, ethylacetate formation, 246
  hydration of olefins, 236
  in isomerization, 261, 262
  methyl alcohol formation, 341
  nitric acid and nitrous gases, 24
  nitric-nitrous acid, 320
  of ammonia synthesis, 307
Esterases, 297
Esterification, 244
  acidolysis, 247
  addition of CO to alcohols or ethers, 248
  alcoholysis, 247
  benzoic acid with alcohol, 178
  butylacetate, 248
  by addition, 245
  catalysts, 246
  cellulose acetate, 249
  direct, 244
  equilibrium, 246
  exchange esterification, 247
  from CO and alcohol, 245
  hydrogen chloride catalyst, 246
  hydrolysis, 77
  ketene, 248
  mercaptans, 247
  oxide catalysts, 247
  starch esters, 248
  vapor-phase, 247
Esters and higher alcohols from oils, 410
  cyclic, depolymerization of, 286
  from nitriles, 245
  from primary alcohols, 248
  hydrogenation of, 233
  hydrogenolysis of, 229
  hydrolysis by enzymes, 297
  hydrolysis of, 238
  velocity of hydrolysis, 239
Estimation of the composition of high-octane gasoline, 19
Ethane from acetylene, 222
  in natural gas, preferential oxidation, 200
  preferential chlorination, 340
Ethanolamine absorbent for CO_2, 364
Ether, addition of CO, 248
  from alcohol, 4, 6
  hydrolysis, vapor phase, 241
Ethers, decomposition of, 68, 105
  hydrogenolysis, 229
  hydrolysis of, 241
Ethyl acetate as negative catalyst, 36
  acetate from acetaldehyde, 325
  acetate, hydrolysis of, 73, 240
  acetate, preparation of, 245
  alcohol, 342
  alcohol, condensation of, 268
  alcohol, conversion into butyl alcohol, 345
  dehydrogenation of, 207
  alcohol from methyl chloride, 235
  alcohol, raw materials for, 388
  amine as catalyst, 300
  benzene, 254, 393
  benzene, dehydrogenation of, 207
  benzene from benzene and ethylene, 253
  benzene from n-octanes and n-octenes, 217
  benzene from polyethylbenzenes, 252
  benzene from styrene, 222
  crotonate, influence of poisons in hydrogenations, 57
  cyanide, 244
  esters from fatty esters, 423
  ether, hydrolysis constant, 241
  fluoride, 250
  hexane from styrene, 225
  methyl ether from ethyl and methyl alcohols, 243
  naphthalene, 256
  nitrite, distilling, 246
  phosphates, formation of, 280
  sulfate, acid, 343
Ethylene, 222
  addition to acids, 245
  addition to benzene, 253
  alcohol from, 343
  chlorhydrin, 394
  compounds, ring closures, 218
  condensation of, 280
  cyanohydrin, 394

Ethylene (*Cont.*):
  derivatives, polymerization tendency, 278
  from hydrocarbons, 373
  glycol from ethylene, 346
  organic acids from, 423
  oxide, 394
  oxide from ethylene, 346
  oxide, hydration of, 346
  oxide, isomerization to acetaldehyde, 265
  polymerization of, 373
  synthetic rubbers derived from, 394
Ethylenic unsaturated group in fatty acids, 410
Evolution of heat on a contact surface, 18
Examination of a contact surface, 92
Exchange of alcohol in ester hydrolysis, 238
  reaction between ethylene and deuterium, 32
  reaction, olefins and deuterium, 100
Exhaustive hydrogenation, 396
Explosion limits, 66
Explosions, branch mechanism of, 46
  in oxidation of paraffins, 197

Factice, 145
Fat hydrolysis, mechanism of, 418
  splitting by alcoholysis, 423
Fats and oils, hydrogenation of, 396
Fatty acids, coloring of, 417, 418, 420
  C_{18}-, natural cis-type, 405
  from Kogasin wax, 336
  from paraffins, 196
  long-chain, ammonolysis of, 295
  production of, 417
Fauser ammonia process, 314
Fenchene, hydrogenation of, 49
Fermentation, alcoholic, 299
Fischer-Tropsch high-pressure process, 330
  synthesis, alcohols from, 344
  synthesis, nickel catalyst for, 160
Fish oils, selective hydrogenation, 404
Fixed catalyst surfaces, 167
  Nitrogen Laboratory U.S.D.A., 315, 316
Flue gases, removal of SO_2 from, 291
Fluid Catalyst Cracking Process, 366
Fluorination, 250
Fluorine carriers, 250
Fluxes, catalytic action of, 111
Foots, carbonization of, 417
  destruction of, 421
Force of cohesion, 75
Formaldehyde from natural gas, 201, 339, 340
  preferential formation, 342
Formic acid from natural gas, 200, 201
  production of, 424
Formvars, 326
Free energy change in hydrogenation of di-isobutylene to octane, 362, 367, 369
  energy change in isomerization, 262
  energy, methyl alcohol formation, 341
  radical mechanism, 251
Freundlich's adsorption isotherm, 84
Fructose, hydrogenation of, 223
Fugacities of isomeric gases, 262
Fumaric acid, 272
Fumaric-maleic acid change, 262
Fuming hydrochloric acid, polymerization of isoprene, 384
Furanoid nucleus, hydrogenation of, 226
Furfural ethyl ether, from diethyl furfural acetal, 229
  from pentoses, 243
  hydrogenation of, 223
  resins, 272
Furfurane, 218
Furfuryl alcohol from furfural, 223, 227
Furnace, continuous catalyst reduction, 153
Fusain, 354

Galactonic acid, mutarotation of, 80
Gas cracking, desulfurization of, 291
  mixtures, 232
  polymerization, 376
Gases for Fischer-Tropsch synthesis, 332
Gasol, 334
Gasoline from different raw materials, properties of, 360
  high-sulfur, desulfurization of, 291
  inhibitors for, 52, 53
  isomerization of, 264

Gasoline (*Cont.*):
  Kogasin I, 337
  production of, from water gas, 151
Gauze catalyst, copper, 385
  catalyst (Pt, Pt-Rh), spectographic control of, 319
Gellivare magnetite, composition of, 150
Gelvas, 326
Generator gas, 332
Geyserite, 144
Glass as catalyst in keto-enol change, 79, 107
Glucamines, from monosaccharides, 294
Glucose from carbohydrates, 238
  hydrogenation of, 223, 230
Glucosidases, 297
Glucosides, hydrolysis by enzymes, 297
Glycerol, 272, 273
  as catalyst in decomposition of HNO_2, 320
  from glucose, 347
Glycocoll as catalyst, 301
Glucol, 272, 273
  mono-esters, 245
Glycols, formation of, 198, 199
  from esters, 233
Glyptal, 272, 273
Gold, colloidal solutions, 132
  sols, decomposition of hydrogen peroxide, 133
Gram-molecule, 11
Graphite as dehydration catalyst, 243
Grignard's agent, 252
  retardation of formation, 36
Growth substances, 14

Haber-Bosch ammonia process, 312
Haemase, effect of poisons on, 54
Hafnium chloride, 257
Halide catalysts for alkylation, activity of, 257
  of alkali or alkaline earth, 424
Halides, 148
Halogen acids as catalysts, 262, 423
  carriers, 249
  compounds, 354
Halogenation, 249
  order of combination, 249
  symposium, 252
Halogens, 148, 354
  as catalyst poisons, 203, 319
Hardwood tar, hydrogenation of, 360
Heat evolved in hydrogenation of oils and fats, 407
  lability of enzymes, 296
  lability of hydrocarbons, 262
  of activation, catalyzed and noncatalyzed reactions, 69
  of activation, decomposition of ammonia, 103
  of activation, decomposition of ethers, 105
  of activation, structural influences, 105
  of activation, true and apparent, 103
  of desorption, 103
  of evaporation (latent), 75
Heavy metals, hydrazine formation, 323
Hecker and Jourdan process, 316
n-Heptane, aromatization, 215
Heterogeneous catalytic chain reactions, 106
  catalytic mechanisms, 85
  catalytic reactions, 81
Hexachlorethane, 328, 340
Hexamethylene, cracking of, 350
  tetramine, condensation agent, 272
Hexane, absorption curve of, 20
Hexane decomposition of, 257
3-Hexene, absorption curve of, 20
Hexyl alcohol, preparation of by Fischer-Tropsch synthesis, 336
n-Hexyl cyanide, 244
High octane numbers, cause of, 363
High-molecular compounds, 275
High-oven gas, 332
High-polymer carriers, 179
High-pressure hydrogenation process, 361
History of catalytic chemistry, 4
Homogeneous catalytic chain reactions, 63
  catalytic reactions, definition, 59
  catalytic reactions, extension of existence of, 16
  gas reactions, 62
  reactions in liquid phase, 70
  reactions, order of reaction, 60
  reactions, reaction rates, 59

Homogeneous (*Cont.*):
  vapor and gas reactions, 67
Homologs of polystyrene polvmers, 285
Homopolar forces, 81
Hopcalite, 8, 194
  catalysts, 172
Hormones, 15
Houdry cracking process, 181, 375
Hycar OR, 392, 394
Hydration, 235
  acetylene, 235, 324
  acetylene, mechanism of, 326
  acetylene, vapor phase, 327
  butylene, 344
  dicyan, 235
  equilibrium, 236
  ethylene, 343
  ethylene oxide, 346
  higher olefins, 343
  mercuric catalysts, 235
  methyl chloride, 235
  olefin oxide, 346
  olefins, 235, 236
  propylene, 344
Hydrazine formation, negative catalysts, 323
  formation of, 323
Hydroamides, hydrogenation of, 231
Hydrocarbon fractions, Fischer-Tropsch low-pressure process, 337
  gases available in U. S. A., 372
Hydrocarbons, aliphatic, alkylation of, 253
  alkylation with alcohols, 258, 259
  alkylation with alkyl chlorides, 258, 259
  alkylation with esters, 258, 259
  alkylation with ethers, 259
  alkylation with olefins, 258, 259
  decomposition of, 257
  dehydrogenation of, 136, 205
  from vegetable fats, 412
  high-molecular weight, decomposition of, 257
  in natural gas, oxidation mechanism, 201
  isomerization of, 264
  natural gas, 200
  radicals from, 348
Hydrocarbons (*Cont.*):
  selective absorption, 378
  slow oxidation, 199
  stability of, 262
Hydrochloric acid as promoter for $AlCl_3$, 255
  acid as sulfonation catalyst, 287
  acid catalyst, 249
  acid, chain mechanism in formation of, 44
  acid formation induced by alkali atoms, 64, 65
Hydrocyanic acid from carbon monoxide and ammonia, 141
  acid from formamide, 141
  acid from nitrogen, hydrogen and CO, 148
  acid, production of, 8
Hydrofining, 361
Hydrofluoric acid, 148
Hydrofluosilic acid as catalyst poison, 319
Hydrogen, 123
  adsorption of, 88
  adsorption on K_2O, 310
  adsorption on palladium, 169
  affinity, 345
  atomic, 308
  content of Raney nickel, 288
  cyanide, formation of, 328, 329
  diffusion through film on contact, 352
  dissociation of, 26
  donor, 298
  donors in hydrogenation, 409
  fluoride, 250
  fluoride in alkylation, 258
  fluoride ring closure catalyst, 218
  for oil and fat hydrogenation, composition of, 406
  formation from steam and natural gas, 363
  from hydrocarbons, 127
  from hydrocarbons, catalysts used, 128
  from water gas, 126
  generation, Bergius process, 126
  generation, steam-iron process, 126
  in desulfurization, 288, 289
  in thermal homogeneous dissociation, 124

Hydrogen (*Cont.*):
  ionization potential, 124
  ions as catalysts, 262
  ions, polymerizing action, 326
  mechanism of oxidation, 30
  peroxide decomposition, 48
  peroxide, decomposition by gold sols, 133
  peroxide; decomposition by iron salts, 190
  peroxide, decomposition by mineral waters, 187
  peroxide, enzymatic decomposition, 300
  p-o conversion, 107
  solubility of, 220
  sources of, 312
  sulfide as catalyst poison, 319
  sulfide as nickel poison, 406
  sulfide, oxidation of, 7
  sulfide, promoter action of, 354
Hydrogenated aviation fuel, tetraethyl lead susceptibility, 366
Hydrogenation, 219
  acetals, 229
  acetone, 223
  acetylene, 222
  alcohols and waxy esters from glycerides, 411
  alcohols as hydrogen donors, 409
  aliphatic and aromatic aldehydes, 208
  alkene linkage, 221
  allyl alcohol, 222
  American coals, 354
  amides (hydrogenolysis), 233
  amines, sec., preparation, 230
  anthracene, 225
  anthroxylon, 355
  attrital matter, 355
  benzaldehyde, 223
  benzene, 224, 234
  benzenoid nucleus, 224
  benzyl alcohol, 228
  bitumen, extracted, 357
  bituminous coal, 355, 357
  borneol, 49
  butyl aldehyde, 326
  camphor, 49
  Canadian coals, 358
  carbon dioxide, 223
  carbon monoxide, 98
Hydrogenation (*Cont.*):
  carbon monoxide, mechanism of, 49, 101
  carbon to carbon bonds, 229
  carbon to metal bonds, 228
  carbon to nitrogen bonds, 230
  carbonyls, 222
  catalysts, ionization potentials, 124
  catalysts, nickel oxides, 154
  catalysts, specification of, 219
  coal, 348
  coal, activity of catalysts, 93
  coal, Bergius process, 353
  coal, factors involved, 352
  coal tars, 353
  coal, wall catalysis, 354
  cobalt, 222
  copper, 222
  copper chromium oxide, 221, 222, 233
  copper chromite, 227, 228
  cracking, 348, 349
  crotonic acid, influence of poisons, 57
  cyanides, 223
  double bonds, —C=C—, 221
  esters, 229, 233
  ethers, 229
  ethyl crotonate, influence of poisons, 57
  ethylene, 222
  exhaustive, 396
  experiments on American coals, 354
  extracted bituminous coal, 357
  fenchene, 49
  fixed nitrogen, 102
  fructose, 223
  furanoid nucleus, 226
  furfural, 223
  glucose, 347
  high-temperature tar, 359
  hydrogenolysis, 228
  imines, 224
  iron, 222
  isooctenes to isooctanes, 374
  lactones, 229
  lignites, 356, 358
  linseed oil, 92
  mechanism, nickel oxide-alumina catalyst, 171
  mild; di-isobutylene, 283
  nickel oxide catalyst, 225

Hydrogenation (*Cont.*):
  nitrogen by microorganisms, 299
  nitrogen to nitrogen bonds, 230
  nitrogen to oxygen bonds, 232
  of cinnamic acid in different solvents, 77
  of trioleine glycerides, 396
  of two-component mixtures, 112
  oils and fats, order of reaction, 407
  oils and fats, velocity of, 407
  oleic acid, 411
  oxygen to carbon bond in alcohols, 228
  palladium on asbestos, 227
  palladium on silica gel, 222
  peat, 358
  phenanthrene, 226
  Pittsburgh seam coal, 354
  plant, oils and fats, formate catalyst, 399, 400
  platinum, colloidal, 222
  production of higher alcohols and esters, 410
  progress, control of, 406
  pyridinoid nucleus, 227
  pyrroloid nucleus, 227
  Raney nickel, 221, 223, 232
  rate, determining factors, 220
  rate of coal, temperature coefficient, 352
  selective, 97, 98
  side reactions, 223
  splint coal, 355
  Stilbene, 222
  Styrene, 222
  symposium, 219
  technical process, 397, 398
  triple bonds between two carbon atoms, 222
  vegetable and animal oils and fats, 396
  West Texas crude, 365
  wood charcoal, 357
  wood tar, 260
Hydrolases, 297
Hydrolysis, 237
  by enzymes, 297
  of cellulose, 238
  of chlorobenzene, 241
  of esters, 238
  of esters, autocatalytic rate, 40
  of esters, mechanism of, 77
Hydrolysis (*Cont.*):
  of esters, structure and velocity, 239
  of esters, velocity constants, 239
  of ethers, 241
  of ethyl acetate, 73
  of fats, rate and mechanism of, 418
  of fats, sulfonic acid catalysts, 420
  of oils and fats, 417
  of oils and fats, autoclave process, 419
  of oils and fats, mechanism of, 417
  of organic halides, 241
  of starch, 6, 238
  of triglycerides, 238
  Twitchell agent, mechanism of, 421
Hydrolytic reactions, 77
Hydroquinone, oxidation of, 298
Hydroxides and oxides, activity in fat hydrolysis, 419
Hydroxy benzyl alcohol, 269
  compounds, hydrazine formation, 323
Hydroxyl radicals, 198
Hydroxylamine, 323
Hydroxylation of unsaturated hydrocarbons, 198
  theory of oxidation, 184

Idrapid, 420, 421
Igniters, gas, 169
Imido esters, acid hydrolysis of, 240
Imines, hydrogenation of, 224
Impure metals, adsorption of gases on, 51
Impurities, effect in solvents, 77
  effect on keto-enol change, 78
  in reactants, 191
  in solvents, 77
  in zinc, 17
Indene polymerization, mechanism of, 285
Induced reactions, 46
Induction period in oxidation reactions, 185, 197
  period in polymerization, 275
  periods, 47
Inductors, 46
Infrared absorption spectra, 19
Inhibition by water, 266
  catalytic effect of iron compounds, 188

Inhibitor formation in oxidation, 196
Inhibitors, 52
  2-amino-5-hydroxy toluene, 53
  p-amino phenol, 53
  p-p′-diamino diphenylamine, 53
  1,5-dihydroxy naphthalene, 53
  for gasoline, 52
  hydroquinone, 53
  in lubricating oils, 196
  pyrogallol, 53
Inorganic vapor-phase reactions, 190
Interionic forces, 74
Intermediary compound, labile, 115
  compounds, in oxidation, 185
  compounds, mercury salts and acetylene, 327
  compounds, oxidation of hydrochloric acid, 194
  compounds, oxidation of sulfur dioxide, 191, 192, 193
  compounds, slow oxidation of hydrocarbons, 199, 200
  formation of carbides in Kogasin synthesis, 334
  halide acids in alkylation, 257
  ion complex, imido ester hydrolysis, 240
  oxidation product, quinone, 203
  reactions, oxidation of ammonia, 216
  sulfonation compound, 286
Intermediate acid formation, 248
  catalyst compound, 36
  compound, NOCN, 69
  compound, peroxide in organic oxidations, 185
  compounds, decomposition of, 200
  compounds in solutions, 62
  compounds, moloxides, 197
  energy-rich states, 42
  esters, 253
  esters in isomerization, 264, 265
  formation of tetrahydrobenzene, 350
  oxides, 328
  oxides, methyl alcohol oxidation, 197
  products, aldehyde peroxide, 197
  products, moloxide, 197
  reaction bodies, 72
  reaction products, 10
  states, formation of nickel aluminate, 110
Intermetallic compounds. See Alloys.
Intramolecular arrangement, catalysis of, 261
Inversion of cane sugar (sucrose), 73, 237
  rate of, 237
Iodine, 148, 304
  as bromine carrier, 250
  as chlorine carrier, 250
  as decomposition catalyst, 67
  carriers, 250
  catalyst for decomposition of ethers, 105
  chloride as iodine carrier, 250
Iodoform and stannous sulfide catalyst, 357
Ionic strength, 72
Ionization potential, hydrogen and hydrogenation catalysts, 124
Ionization, thermal, of N_2 and O_2, 305
Ipatieff's rule of addition of olefin to an acid, 265
Iridium, 319
  salts, 169
Iron, 310, 322
  activated with copper, 331
  adsorption of hydrogen on, 39
  allotropic change, 123
  allotropic forms, 82
  alumina alloy catalysts, 150
  alumina potassium oxide catalyst, 310
  and iodine catalyst, 357
  and iron salts as oxidation catalysts, 187
  carbide, 321
  catalyst in amination, 292
  catalyst in desulfurization, 289
  catalyst, reduced, 150
  catalyst surfaces, 30
  catalysts, chemical analysis and activity, 31
  catalysts containing alumina and potassium oxide, 51
  catalysts, mixed, 335
  chloride, 151
  compounds in soils, 323
  condensation catalyst, 268
  evaporated films on glass, 33
  filings, 308
  for generation of hydrogen, 125
  in paint driers, 151

Iron (*Cont.*):
  minerals, spectrographic analysis of, 11, 12
  oxidation catalyst in nature, 151
  oxide, 312, 327
  oxide catalyst, 357
  oxide catalysts, preparation of, 150
  oxide granules, Al_2O_3-K_2O promoted, 315
  oxide hydration catalyst, 327
  oxide, Luxmasse, 348
  oxide, magnetic, CaO-MgO, ammonia catalyst, 313
  oxide on active alumina, 177
  oxide, reduction of, 126, 150
  oxides, desulfurization of coke oven gas, 288
  pentacarbonyl, anti-knock, 108
  powder, alkali cyanide formation, 323
  shavings coated with K_2CO_3, 330
  tube for dehydrogenation, 210
  turnings, activated, 314
  very pure, spectrographic and chemical analysis of, 12
Isoborneol, dehydrogenation of, 206
Isobutane, aromatization, 217
  use of, 379
Isobutene, formation of, 281
Isobutenes, polymerization of, 373
Isobutenol, dehydrogenation of, 208
Isobutyl alcohol from lower alcohols, 345
  alcohol from pentaerythritol, 230
  cyanide, 244
  mercaptan, desulfurization of, 289
  sulfide, desulfurization of, 289
Isobutylene, absorption in sulfuric acid, 282
Isocel, 181
Isohexane, use of, 379
Isomerization, 261
  alumina catalyst, 264, 265
  conjugation assays, 263, 264
  drying and semi-drying oils, 263
  equilibrium, 261
  ethylene oxide—acetaldehyde change, 265
  free energy change, 262
  freedom of motion of atoms, 262
  fugacity of isomeric gases, 262
  gaseous, 261
Isomerization (*Cont.*):
  heat of formation of isomers, 262
  hydrocarbons, mechanism of, 264
  intermediate esters in, 264
  isopropyl ethylene, 264, 265
  maleic—fumaric acids, 262
  metameric catalytic transformation, 265
  of isopropyl ethylene into ethyl ethylene, 264
  of petroleum feeds, 363
  oleic—elaidic acids, 263, 405
  ordinary, 265
  reaction mechanisms, 265
  stability of hydrocarbons, 262
Iso-octane from di-isobutylene, 283
Iso-octane production, 376
Iso-oleic acid, formation during hydrogenation, 404, 405
Iso-olefins, quality of oils, 406
Isoparaffinic compounds, 260, 261
Isoparaffins and olefins, reaction of, 259
Isopentane, use of, 379
Isophthalic acid diethyl ester, alkaline hydrolysis, 240
Isoprene, 384
  from acetylene and acetone, 385
  from branched pentenes, 206
  from cresol or phenol, 385
Isopropyl alcohol, 210
  alcohol, formation of, 268
  alcohol from propylene, 344
  naphthalene, 256
Isotherms, adsorption, 84
Isotopes, 123
  exchange reaction of deuterium, 32

Joint catalytic action, 171

Keeping quality of hydrogenated products, 403
Ketene, 248
  production, 244
Keto-enol change, 77
  catalysts for, 107
  catalytic influences on, 14
  of methylbenzoyl glyoxal, 79
  of phenylbenzoyl glyoxal, 79
Ketone, symmetrical, formation, 211
Kieselguhr, 152, 335
  as dehydration catalyst, 244

Kinetics of acid-base catalysis, 72
  of hydrogenation, 351
Knocking in combustion engine, 108
Kogasin, 332
  catalysts, 334, 335
  gases for making, 333
  synthesis, 334
Kogasin I, gasoline, 337
Kogasin II, Diesel oil, 337
Kontaktspalter, 420, 421
Korogel, 391

Laboratory reagents, purity (composition) of, 13
Lactone formation, autocatalytic rate, 40
Lactones, hydrogenolysis of, 229
Langmuir's adsorption isotherm, 84
Latex, synthetic rubber, 395, 396
Law of mass action, 261
Lead, 141
  chamber process for oxidation of SO_2, 192
  oxide, reduction of, 141
  tetrabenzyl, hydrogenolysis of, 228
  tetraethyl, anti-knock properties of, 38
Lighters, cigar and cigarette, 169
Lignin, 247
Lignite coke for making Kogasin, 333
Lignites, hydrogenation of, 356
Linkage, alkene, 221
Linoleic acids (9,12 and 9,11) in castor oil, 412
Linseed oil, autoxidation of, 39
  oil, boiled, 39
  oil, exhaustively hydrogenated, 397
  oil, hydrogenation of, 92
  oil, 9,11-oleic acid in, 413
Lipases, 297
Liquefaction of air, 315
Liquefied air, fractional distillation of, 311
Liquid fuels from natural gas, 339
Liquid phase destructive hydrogenation, 353
  phase, homogeneous reactions in, 70
Lithium, 129
Loss of catalyst during operation, 164
Low-pressure hydrogenation process, 367
Lubricants by dechlorination of chlorinated hydrocarbons, 251
Lubricants by Fischer-Tropsch synthesis, 337
Lubricating oils, 361
  oils from chlorinated Kogasin, 338
  oils, natural inhibitors in, 196
  oils, synthetic, from ethyl naphthalenes, 256
Lysalbinate of sodium, 169

Magnesia, carrier, 215
  tubes as support for nickel catalysts, 160
Magnesium chloride, 412
  compound catalysts, promoted, 345
  oxide, 412
  oxide as desulfurization catalyst, 291
  oxide carriers, 176
  oxide catalyst, promoted, 345
  sulfite, formation and properties of, 291
Magnetite as ammonia catalyst, 150
Maleic acid, 272
Maleic anhydride from benzene, 203
Maleic—fumaric acid change, 262
Manganese, 310, 322, 323, 335
  acetate, 149
  acetate, oxidation of acetaldehyde, 325
  carbonate, 149
  dioxide, 149, 327
  dioxide catalyst, mixed, 304
  dioxide, in oxidation catalyst, 172
  in paint driers, 152
  nitrate, 304
  oxide, 149, 322
  vanadate, 149
Manganous oxide, 342
  oxide and chromium oxide, adsorption on, 88
Mannitol from fructose, 223
  hydrogenation of, 230
Marine oil, hydrogenation of, 404
Mass action law, 296
Mass spectrograms, 21
Mass spectrometer analysis, 25
  spectrometer, installation of, 23
Mass transfer, 247
  transfer, rate of, 34

Material or chemical chain reactions, 41
Maxted hydrogenation column, 401
Mechanism of isomerism in hydrocarbons, 264
Mechanisms, heterogeneous catalytic, 85
Menhaden oil, hydrogenation of, 404
Mercaptans, decomposition of, 288
  esterification of, 247
  in petroleum feeds, 379
Mercuric chloride, reduction of, 46
  salts, hydration catalysts, 235
Mercury, 135
  as fluorination catalyst, 135
  catalyst, 325
  salts, intermediary compounds with acetylene, 327
Metal alkyls, 252
  catalysts for oxidation of natural gas, 340
  films, evaporated, on glass, 33
Metallic lattice forces, 81
  soaps, influence on catalyst, 403
Metals, allotropic changes in, 122
  catalytic effects on hydrocarbons, 116
  colloidal, 166
  colloidal, as antiknock compounds, 108
  diffusion of hydrogen through, 124
  impure, gas adsorption on, 51
Metameric catalytic transformation, 265
Methane, chlorination of, 251
  from CO, 329
  in hydrogen cyanide synthesis, 321
  oxidation of, 109, 199
  water gas from, 338
p-Methoxy-phenylamino acetic acid as catalyst, 301
Methyl acrolein from isobutenol, 208
  alcohol catalyst, 176
  alcohol decomposition, 107
  alcohol from carbon monoxide, 341
  alcohol from natural gas, 200, 201, 340
  alcohol from water gas, equilibrium, 341
  alcohol, oxidation of, 7
  alcohol production, catalytic, 8
Methyl (*Cont.*):
  alcohol, reaction with water, mechanism of, 106
  alcohol, synthetic, 340
  amine as catalyst, 300
  benzoyl glyoxal, keto-enol change of, 79
  chloride, 340
  chloride from methane, 251
  chloride, hydration of, 235
  cyanide, 244
  cyclohexanol, 385
  cyclopropane, 281
  esters from fatty acids, 423
  ether, 243
  ether, decomposition of, 68
  ethyl ketones, unsaturated, synthesis of, 267
  formate, preferential formation, 342
  isobutyl carbinol, 210
  isobutyl ketone, 210
  isopropyl ether, decomposition of, 68
  octenyl ketone, synthesis of, 267
  rubber, 391
  vinyl ketone from butene-1-ol-3, 208
1-Methyl butadiene, 384
2-Methyl butadiene, 384
1-Methyl-3-aminooxindol as catalyst, 302
Methylene glycol, 269
  radical, 335
Methylol methylene urea, 274
Mineral waters, catalytic action of, 187
Minor constituent, 15
Mixed catalysis, 79
  catalysts, 170
  catalysts, fat hydrolysis, 419
  catalysts, heat stability of, 342
  catalysts, Kogasin synthesis, 335
  cobalt catalysts, 335
  copper catalyst, 209
  copper-cobalt catalyst, 347
  copper-nickel catalyst, 347
  iron catalysts, 335
  manganese dioxide catalyst, 304
  molybdenum catalysts, 171
  nickel and copper carbonates, 409
  nickel catalysts, 335
  nickel oxide, alumina catalyst, hydrogenation mechanism, 171

Mixed (*Cont.*):
  oxides, 319
  zeolite, 176
Mixtures as a concept of composition of matter, 16
  catalysis in, 111
  compounded, 109
Moisture and reactivity, 376
  as promoter in oxidation of CO, 172
Molcohesion, 75
Molecular addition compounds, 62
  forces, 81
  weight of castor oil, 414
  weight of catalases, 296
  weight of natural rubber, 387
Molybdenum, 310, 323
  as growth substance, 14
  catalysts, mixed, 171
  dehydration of castor oil, 416
  esters and alcohols from oils, 411
  sulfide, 147, 354
  trioxide, 147, 203
  trioxide and stannous sulfide catalyst, 357
  trioxide, hydration catalyst, 327
Monoethyl amines by desulfurization, 288
Monomethylol urea, formation of, 273
Monomolecular layers on catalyst surfaces, 28, 31, 32
Monosaccharides, glucamines from, 294
Mont Cenis (Uhde) ammonia process, 314
Montmorillonite, activated, 180
  magnesium-substituted, 180
Motor fuel, chain reactions in combustion of, 108
  fuel from wood tar, 360
  gasoline, 361
Multiple adsorption, 99
  binding, 99
Mutarotation of galactonic acid, 80
  of sugars, 79

Naphthalene, alkylation of, 256
  destructive hydrogenation, 363
  ethyl, 256
  stearosulfonic acid, 420
Naphthas, low aniline point, high solvency, 361
Naphthenes, 280
  alkylation with ethylene, 255
Nascent hydrogen, diffusion through metals, 124
Nash Hytor blower, 324
Natural aviation fuel, tetraethyl lead susceptibility, 366
  composition, 15
  gas, 339
  gas as source for Fischer-Tropsch synthesis, 338
  gas, chemicals from, 339
  gas, chlorination of, 340
  gas for Kogasin synthesis, 333
  gas, formaldehyde from, 339
  gas, liquid fuels from, 339
  gas, metal catalysts for oxidation of, 340
  gas, methyl alcohol from, 200, 201, 340
  gas, oxidation, 200
  gas, water gas from, 338
Nature and properties of catalysts, 115
Negative catalysis, 35
  catalysis, sulfuric acid, sulfates, 320
Neoprene, 386
Neutral salts as catalysts, 246
Nickel, 152, 310, 322
  allotropic change of, 123
  allotropic forms, 82
  as dehydrogenation catalyst, 208
  carbide, 101, 322
  carbonate, 152, 153, 408
  catalyst, 329
  catalyst, activator for, 160
  catalyst, consumption of, 408
  catalyst, esters and alcohols from oils, 410
  catalyst, exchange reaction between ethylene and deuterium, 32
  catalyst, hydrogenation/dehydrogenation, 205
Nickel catalyst, hydrogenation of carbon monoxide, 101
  catalyst in desulfurization, 289
  catalyst, motor fuels, 362, 367, 374, 376
  catalyst poisons (CO, O_2), 58

Nickel (*Cont.*):
  catalyst promoted with alumina, mechanism of, 48
  catalyst promoted with various oxides, 49, 50
  catalyst, supported, 98
  catalyst, water formation, 104, 118
  catalyst, water gas from methane and natural gas, 338
  catalysts, activity of, 92
  catalysts, mixed, 335
  catalysts, poisoning of, 55
  catalysts promoted with thoria, 51
  chromate, reduction of, 147
  chromium catalyst, 147
  copper catalyst, 402
  copper zincate, esters and alcohols from oils, 411
  evaporated films on glass, 33
  formate, 408
  formate, reduction of, 155
  glyceride hydrogenation, 411
  hydroxide, 409
  magnesium alloy, 158
  metal, 408
  nitrate, 408
  nitrate, composition of, 153
  nitrate, hydrogenation catalysts from, 153
  on porcelain, motor fuels, 369
  on pumice, 343
  oxide, 408
  oxide alumina catalyst, hydrogenaation mechanism, 171
  oxide catalyst, 225
  oxide on active alumina, 177
  oxides, 153
  oxides as hydrogenation catalysts, 154
  oxides, reduction of, 154
  oxides, stoichiometrical formulas, 154
  promoted, 331
  pyrophoric, 154
Nickel, Raney, 98, 221
  regenerated catalyst, 409
  selectivity, 96, 98
  subsulfide, preparation of, 291
  sulfate, 408
  sulfate, composition of, 152
  very pure, spectrographic analysis of, 13
Niobium chloride, 257
Nitrates, catalysts from, 131
Nitric acid, fuming, oxidation mechanism, 188
  acid and nitrous acid equilibrium, 320
  acid and nitrous acid, increase of oxidizing power, 188
  oxide and cyanogen, reaction between, 69
  oxide as catalyst, 304, 340
  oxide, equilibrium, 305
Nitride formation of Ba, Ti, Si, and Al, 310
Nitride theory of ammonia catalysis, 102
  compounds, hydrogenation of, 232
Nitrobenzene, amination of, 291
  adsorption on catalyst surfaces, 32
Nitrogen, adsorption on K_2O, 310
  atomic, 308
  chemisorption on tungsten, 102
  dioxide, equilibrium, 305
  dioxide, industrial process, 306
  fixation, mechanism of, 170
  fixed, hydrogenation of, 102
  free, from ammonia, 318
  from producer gas, 311
  industry, 304
  oxides, 304
  oxides as oxidation catalysts, 6
  oxides, kinetics of, 305
  pentoxide, decomposition, mechanism of, 307
  pentoxide, equilibrium, 306
  to nitrogen bonds, hydrogenation of, 233
  to oxygen bonds, hydrogenation of, 232
  trioxide, equilibrium, 305
  trioxide, formation of, 307
Nitroparaffins, condensation of, 268
m-Nitro-phenylamino acetic acid as catalyst, 301
Nitroso compounds, hydrogenation of, 232
Nitrosulfonic acid, 192
Nitrosyl sulfuric acid, 192, 193
Nitrous acid as catalyst, 263
  oxide, continuous process for, 304
  oxides, oxidation of SO_2, 192

Nucleic acids, hydrolysis by enzymes, 297

Octadecane, 337
Octahydro anthracene sulfonic acid (Idrapid), 420
Octane numbers of various octanes, 373
  product, properties of, 371
Octanes, antiknock value of, 373.
Octanes, hydrogenation of, 362, 367, 369
Oils and fats, hydrogenation of, 396
  by dechlorination of chlorinated hydrocarbons, 251
Olefin formation in Fischer-Tropsch synthesis, 337
  oxide, hydration of, 346
Olefins and isoparaffins, reaction of, 259
  condensation by acids, 280
  dehydrogenation, 205
  from paraffins, 375
  hydration catalysts for, 235, 326
  polymerization of, 279
Oleic acid, hydrogenation of, 396, 397, 411
  elaidic acid isomerization, 263, 405
Olive oil, exhaustively hydrogenated, 397
Opalite, 144
Oppanol, 391
Order of combination, 249
Organic acids from alcohols, 209
  esters from ketene, 248
  halides, hydrolysis of, 241
  liquid-phase reactions, 194
  oxidation reactions, 194
  peroxides, chlorination catalysts, 251
  substances, catalytic action of, 14
  sulfur compounds, nickel poisons, 406
Orthophosphoric acid as dehydration catalyst, 242
  acid on pumice as dehydration catalyst, 244
Oscillations in periodic change, 113
Osmium, 310, 319
  tetroxide, 169
  tetroxide catalyst, 198
Oxalic acid, 272
  acid, decomposition by anhydrous sulfuric acid, 36
  acid, from wood and cane sugar, 189
Oxamide from dicyan, 236
Oxidases, 299
Oxidation, 184
  acetaldehyde, 298, 325
  alcohols, 184
  alcohols to aldehydes, 202
  aldehydes, 184
  aldehydes to acids, 198
  alkyl benzenes, of, 194
  ammonia, 316
  ammonia, catalyst for, 163
  aniline, 189
  anthracene, 141, 204
  aromatic compounds, 202
  benzene, 203
  carbon monoxide, 194
  carbon monoxide at room temperature, 8
  carbon monoxide on platinum, mechanism of, 29
  catalyst of base metal plus rare earth oxide, 131
  catalysts, 169
  catalysts, copper-vanadyl zeolite, activation, 175
  catalysts from cerium, 138
  catalysts, osmium, 169
  catalysts, ruthenium, 169
  chain reactions, 187, 189, 190
  characteristics of hydrocarbons, 195
  cupric/cuprous oxides/copper mechanism, 187
  drying oils, catalysts for, 196
  ethylene to glycol, 346
  ferrous ions as catalyst, 187
  hydrocarbons, saturated, long-chain, 194
  hydrocarbons, slow, 199
  hydrochloric acid, 193
  hydrogen at high and low pressures, 64
  hydrogen on platinum, mechanism of, 30
  hydrogen sulfide, 8
  hydroquinone, 298
  hydroquinone, electron reaction, 298
  hydroxylation theory, 184

Oxidation (*Cont.*):
  induction in, 185
  inhibitor formation in, 196
  inorganic reactions, 186
  intermediate compounds, 185
  iron and iron salts as catalysts, 187
  labilization of hydrogen, 186
  mechanism, ammonia, 317
  mechanism, hydrocarbons in natural gas, 201
  mechanisms, 185
  methane, 109, 199
  methane, mechanism of, 184
  methyl alcohol, 201, 202
  naphthalene, 189, 203
  naphthalene to phthalic acid, 141
  natural gas, 200
  natural gas, formation of formaldehyde, 339, 340
  nitric oxide, mechanism of, 306
  olefin oxides, formation of, 346
  paraffins, catalysts for, 197
  paraffins, mechanism of, 197
  paraffins to fatty acids, 196
  peroxide formation, intermediary, 194
  phosphorus, 193
  preferential, ethane, 200
  rate of, 195
  reduction mechanism, enzymes, 298
  selective, 99
  sugars, 188
  sulfur dioxide, mechanism, 87, 191
  sulfur dioxide, MnO_2 catalyst, 291
  theory, Frankenburger, 186
  theory, Wieland's, 186
  toluene, 203
  vapor-phase, 199
Oxide catalysts, action on methyl alcohol, 209
  catalysts, dehydrogenation, 375
  catalysts for decomposition of nitrous oxide, 304
Oxides, basic, of CaO, MgO, and ZnO, in fat hydrolysis, 419
  catalytic behavior of, 209
  metal, 248, 340
  metal, electrons, 350
  mixed, 319
Oxidized paraffin as catalyst, 196
Oxido-reductases, 298
Oximes, hydrogenation of, 232
Oxygen, activated adsorption on silver, 89
  as negative catalyst, 36
  as polymerization catalyst, 284
  film on tungsten filament, 27
  nickel poison, 369
  poison action of, 213
  promoter in p-o-hydrogen conversion, 107
  removal in coal hydrogenation, 352
  to carbon bond in alcohols, hydrogenolysis of, 228
  trace, as promoter, 69
  true volume of, in different compounds, 120, 121

Paal's catalyst method, 169
Palladium, 310, 319
  catalysts, 168
  colloidal, 169
  on asbestos, 227
  poisoning by hydrogen sulfide, 56
  wire, catalytic action of, 26
Paraffinic kerosenes, water-white, 361
Paraffins, conversion to olefins, 375
  dehydrogenation, 375
  higher, alkylation of, 255
  lower, utilization of, 377
  separation probabilities, 276
  straight-chain, cracking of, 350
Paraldehyde, depolymerization of, 285
  formation of, 326
Para-ortho-hydrogen conversion, 107
Parinaric acid, 20
Partial reactions, oxidation of ammonia, 316
Particle size, platinum preparations, 164
Path of reaction, 329
Peak atoms, 33
Peanut oil, hydrogenation of, 404
Pentadecane, 337
Pentaerythritol, hydrogenation of, 230
Pentane, 2,2,4-trimethyl, 283
Pentaphenyl ethane, hydrogenation of, 229
n-Pentyl cyanide, 244
Pepsin, crystallized, activity of, 303
Peracetic acid, formation of, 327
Perbunan, 387, 394
  extra, 391

Perchloric acid as alkylation agent, 254
Perduren G, 392
Perhydroanthracene, 225
Perhydrophenanthrene, 226
Perilla oil, 9, 11
  oil, oleic acid in, 413
Periodic catalysis, 113
  reaction changes, 112
Peroxidases, 299
Peroxide formation in combustion, 108
Perylene from α-dinaphthyl, 217
Petroleum, sulfur compounds in, 289
Pfeilring, 420, 421
Phase-boundary catalysts, 81
Phases, 82
Phenanthrene, hydrogenation of, 226
Phenol as inhibitor, 52
  chlorobenzene, 241
  formaldehyde condensation, 269
  from acetylene, 329
  reduction of, 228
  resinoids, 271
  stearosulfonic acid, 420
Phenols, alkylation with olefins, 254
  condensation with acetylene, 135
  exchange with alcohols in esters, 247
  reaction with isobutylene, 256
Phenyl-amino acetic acid as catalyst, 301
1-Phenyl-3-amino-oxindol as catalyst, 302
Phenyl-benzoyl glyoxal, keto-enol change of, 79
Phenyl ethyl cyanide, 244
Phenylether, formation of, 255
1-Phenyl-3-methylpyrazolone-5, hydrogenation of, 233
Phenyl-α-naphthylamine, 52
Philosopher's Stone, 4
Phosphate catalysts for decomposition of NH_4NO_3, 304
Phosphine as catalyst poison, 319
Phosphoric acid, 141
  acid, addition of isobutylene to, 254
  acid, alkylation catalyst, 254
  acid catalyst, deuterated, 282
  acid, condensation catalyst, 280
  acid, dehydration of castor oil, 414
Phosphoric (*Cont.*):
  acid, polymerization of olefins, 373
  acid, solid, 243
  acid (U. O. P.) polymerization catalyst, 376
Phosphorus as iodine carrier, 250
  pentoxide, 254, 340
  pentoxide, promoter action, 287
  poison for ammonia catalyst, 311
Phosphoryl chloride, promoter action of, 287
Phosphotungstic acid catalyst, 246
Phthalic acid, 272
  acid diethyl ester, alkaline hydrolysis of, 240
  acid esters, alkaline hydrolysis, 239
  acid production of, 7
  anhydride, 203, 273
Physical or energy chain reactions, 41
Picoline, 217
Piperidine as catalyst, 266
Piperidine, from pyridine, 227
Piperylene, 384
Pittsburgh seam coal, 351, 354
Platinized carbon, 217
Platinum, 310
  black, 164
  black, hydrogenation of crotonic acid, 57
  black, p-o-hydrogen conversion, 107
  catalyst, 6, 316
  catalyst, supported, 167
  catalysts, 162
  colloidal, 164
  colloidal, effect of poisons on, 54
  foil, 319
  gauze, 317, 319
  group metals, 162
  group metals, impurities of, 162
  rhodium alloys for ammonia oxidation, 190
  rhodium gauze, 319
  sponge, 164
  vanadium catalyst, 144
  wire, catalytic action of, 26
Poison effect nullified, 311
  oxygen, 213
  water vapor, 213
Poisoning of dehydrogenation catalyst, prevention of, 208
  of Fischer-Tropsch catalysts, 332
  of Kogasin catalysts, 336

Poisoning (*Cont.*):
  osmium oxide fumes, 169
Poisons, ammonia catalysts, 311, 319
  catalyst sensitivity, 154
  catalyst, sulfur, 145
  catalyst, 54
  CO and O_2 on metal films, 33
Polyalcohols from carbohydrates, 347
Polymerization, 275
  butadienes, 384
  butene, 373
  butylenes, 282, 367
  catalysts, 278, 279, 386
  catalysts, frequency of use, 279
  chain reaction, 275
  classification of high-molecular compounds, 275
  copolymers, 284
  definition, 255
  ethylene, 280, 373
  indene, 285
  isobutene, 373
  kinetics, 280
  olefins, 280, 373
  polystyrene, polymer homologs, 285
  pressure, 278
  process, motor fuels, 372, 374
  propene, 373
  radiation, 278
  styrene, 284
  synthetic gasoline, 337
  temperature, 278
  tendency, 278
  unsaturation, 276, 277
  vinyl chloride—vinyl acetate, 284
Polymerizing action, hydrogen ions, 326
Polymers from isobutylene, 283
Polyvinyl derivatives, 283
  resins, 326
Positive catalysis, 35
  catalysts, 10
Potassium bisulfate, 243
  cyanate, 249
  cyanide as catalyst poison, 55
Precharging catalysts of the 8th group, 118
Precipitated catalysts, 335
Preparation of alcohols, 340
  of catalysts, alumina, 136
  of catalysts, alumina carrier, 177

Preparation (*Cont.*):
  of catalysts, alumina, supported, 138
  of catalysts, basic nickel carbonate, 152
  of catalysts, carbon, activated, 139
  of catalysts, chrome—alumina, 137
  of catalysts, copper, 130
  of catalysts, copper—chromium oxide, 131, 145
  of catalysts, copper—vanadyl zeolite, 175
  of catalysts, copper—zinc, 132
  of catalysts, copper—zinc oxide, 134
  of catalysts, Hopcalite, 172
  of catalysts, hydrogen, 125, 126, 127
  of catalysts, iron, 150
  of motor fuels, 360
  of nickel-alloys, 158
  of nickel-aluminum alloy, 158
  of nickel-calcium alloy, 158
  of nickel, Fischer-Tropsch, 160
  of nickel formate, 155
  of nickel nitrate, 153
  of nickel oxides, 154
  of nickel silicon alloy, 158
  of nickel sodium alloy, 158
  of nickel, supported, 160
  of palladium, colloidal, 166
  of platinum black, 165
  of platinum oxide, Adam's, 165
  of Raney nickel, 158
  of silica gel, 140
  of silver, 132
  of trimethyl ethylene, 265
  of vanadium, 142, 143
  of vanadyl hydroxide, 174
  of zeolite, 176
Pressure, polymerization, 278
Producer gas, composition of, 312
Promoted iron catalyst, 308
Promoter action, alkali in Kogasin catalysts, 335
  action, copper in Kogasin catalysts, 335
  action, graphic illustration of, 50
  action, hydrochloric acid, 256
  action, hydrogen sulfide, 354
  action, moisture, 172, 211
Promoters, 48
  for sulfonation, 287
  function of, 335

Promoters (*Cont.*):
  oxygen, p-o-hydrogen conversion, 107
Propanol-2 from acetone, 223
Propene, polymerization of, 373
Propyl alcohol from allyl alcohol, 222
  alcohol from propylene, 235
  cyanide, 244
  sulfide, desulfuration of, 289
Propylene, addition to benzene, 253
  glycol from glucose, 347
  hydration of, 235
Protalbinate of sodium, 169
Proteases, 297
Proteins, hydrolysis by enzymes, 297
Protolytic reaction, 71
Proton donor, 71
Pulsating catalysis, 113
Pumice as dehydration catalyst, 243, 244
  support for nickel catalyst, 160
Pure substances, reactivity of, 10
Purification of water gas, 330, 331
Purity and periodic changes, 113
Pyrex glass, wall of converter, 353
Pyridine as catalyst, 249
  hydrogenation of, 227
6,7-Pyridino-3-amino-oxindol as catalyst, 302
7,6-Pyridino-3-amino-oxindol as catalyst, 302
Pyrocathecol as inhibitor, 52
Pyrolytic polymer gasoline, properties of, 377
Pyrophoric nickel, 154
Pyrrole, 217
  hydrogenation of, 227
Pyrroles, Knorr synthesis of, 232
Pyrrolidine, from pyrrole, 227

Quinoline as catalyst, 249
Quinone from hydroquinone, 298
  intermediary oxidation product, 203

Radiations, polymerization, 278
Radical formation, methylene, 335
Radicals from hydrocarbons, 348
  hydroxyl, 198
Rancidity of oils and fats, 36
Raney catalysts, 158
  nickel, 98, 221, 223, 227, 232
  nickel, hydrogen content, 288
Raney (*Cont.*):
  nickel in desulfurization, 288
Raschig rings, catalytic action, 347
Rate of desorption, equation, 91
  of hydrogenation, determining factors, 220
  of inversion, 237
  of mass transfer, 34
  of oxidation, 195
  of surface reaction, 34
Reaction media, catalytic effect of, 1
  path, 98
  paths of compounds from CO and H_2, 329
  products, negative catalysis by, 37
  rate, collision theory, 61
  rate of catalyst poisoning, equation for, 58
  sphere, 62
Reactor corrosion by $AlCl_3$, 181
Recycling plants for oil hydrogenation, 401
Reduction of cobalt oxide, 151
  of copper oxides, 130, 134
  of copper-vanadyl zeolite, 175
  of Fischer-Tropsch nickel catalyst, 160
  of iron oxide, 126, 150
  of lead oxide, 141
  of nickel chromate, 147
  of nickel formate, 155
  of nickel oxides, 154
  of supported chromic acid, 175
  of supported nickel catalyst, 160
  of vanadic acid, 174
Reforming, 375
Regeneration of dehydrogenation catalysts, 137
  of Kogasin catalysts, 336
Removable components in alloys, 172
Report of the Baruch Committee, 388
Repression of undesirable reactions, 59
Residual forces, 81
Resin formation from phenol and formaldehyde, 270
Resinox, 269
Resins, infusible, 272
  insoluble, 272
  polyvinyl, 326
Retardation of chemical reactions, 36
  of oxidation of drying oils, mechanism of, 196

Reversible processes, catalysis in, 35
Rhenium, 149, 209
  catalyst for dehydrogenation, 208
Rhodium, 169, 319
Ring closure catalyst, hydrogen fluoride, 218
  closure, α-dinaphthyl, 217
  closures, acetylene compounds, 217
  closures, catalyst for, 217
  closures, ethylene compounds, 218
Ruthenium, 169, 319

Saccharase, 299
Safety fuels, 361
Saligenins, 270
Salt effect, primary and secondary, 73
  effects, 72
Salting out, Twitchell agent, 421
Salts, acidic, 248
  as catalysts, 343
Samarium oxide, 132
  oxide, promoter for silver catalysts, 202
Sand as dehydration catalyst, 243
Secondary alcohols, dehydrogenation of, 208, 210
  center in chain reactions, 44
Sedol, 326
Selective absorption of hydrocarbons, 378
  absorption of isobutylene in acid, 282
  hydrogenation of diisobutene, 98
  hydrogenation of vegetable oils, 404
  oxidation, 99
  polymerization of olefins, 373
Selectivity, 95
  copper catalyst, 342
  enzymes, 295
  hydrogenation, 97, 98
  hydrogenation catalyst, 220
  of catalysts, 1
  of copper chromite, 95, 96
  of nickel, 96, 98
  of triglyceride hydrogenation, 403
  organic catalytic reactions, 329
  zinc oxide catalyst, 342
Selenium compounds as catalyst poisons, 319
Semi-drying oils, linkage shifts, 263
Sensitivity of catalysts to poisons, 154
Separation probabilities, paraffins, 276
Shawinigan Falls, 324
Shortening, iodine values, 405
Side chains in cracking of aromatics, 349
  reactions, hydrogenation of cyanides, 223
Silica alumina reforming catalyst, 375
  gel, 140, 335
  gel, adsorption of nitrogen on, 32
  gel catalysts, 246, 247
  gel, oxidation of nitric oxide, 306
Silicon carbide as dehydration catalyst, 244
  carbide carrier, 178
  hydride as catalyst poison, 319
Silver and alumina, oxidation catalysts, 346
  catalyst, water formation, 104
  catalyst with samarium oxide, 202
  catalysts, 132
  nitrate, 304
  oxide, 132
  oxide in oxidation catalysts, 172
  oxide, reduction of, 132
  reduced, as oxidation catalyst, 346
  salts, organic, on active charcoal, 346
  salts, organic, on silica gel, 346
Simple hydrogenation, motor fuels, 362
Simultaneous catalysis, 79
Sintering, 310
  copper catalyst, 207
  decay of catalyst by, 59
  of Kogasin catalysts, 336
Soaps, metallic, influence on copper-nickel catalyst, 403
Sodium, 129
  acetate as catalyst, 248
  alcoholate as catalyst, 247, 248
  carbonate as condensing catalyst, 268
  catalyst, 247
  hydroxide, fat hydrolysis, 419
  metal catalyst, 387
  oleate as emulsifier, 386
  thiosulfate as catalyst, 262
Solids, catalysis in, 109
Solution, ionic strength, 72
Solvent, by high-pressure hydrogenation, 147
  effect, polymerization, 279

Solvents, acid-base nature of, 75
  catalytic nature of, 75
  chemical nature of, 75
  formation of, 287
Sorbitol from glucose, 223
  hydrogenation of, 230
Sovprene, 391
Soybean oil, decomposition of, 412
  oil, hydrogenation of, 402, 404
  oil, 9,11-oleic acid in, 413
Space-time yield, 95
Spatial position, 61
Specific gravity of normal chlorinated paraffins, 338
  types of catalytic reactions, 184
Spectra, ultraviolet absorption, 264
Spectrometric mass analysis of a gas mixture, 24
Spectroscopic methods in catalytic technique, 19
Spent catalyst, 366
Splint coal, hydrogenation of, 355
Stability of hydrocarbons, 262
Standard composition, 15
Stannous oxide catalyst, 358
  sulfide, 351, 354, 355
  sulfide and molybdic acid catalyst, 355, 356, 357
Starch esters, 248
  hydrolysis, 238
Stationary state, 42
Steam-iron process for generation of hydrogen, 126
Stearic acid, catalytic preparation of, 396
Steric factor in polymerization, 275
Stilbene, hydrogenation of, 222
Strain action, 99
Structure of catalyst and reactivity, 32
  of hydrocarbons and aromatization, 214
  of synthetic rubbers, 391
Styrene, 393
  from ethyl benzene, 207
  hydrogenation, 222, 225
  polymerization, 278
  polymerization mechanism, 284
  potential U. S. supply, 388
Sub-bituminous coal, hydrogenation of, 356
Substitute for tung oil, 412
Successive reaction stages, 10
Sucrose, inversion of, 237
Sugars, decomposition of HNO_2, 320
Sulfate ion, retarding action, 320
Sulfates, acid alkali, dehydration of castor oil, 414, 415
  dehydration of castor oil, 416
Sulfite solutions, autoxidation of, 189
Sulfites, oxidation of by atmospheric oxygen, 36
Sulfonation, 286
  anthraquinone, 286
  benzoic acid, benzene, and higher alcohols, 287
  catalysts, 286
  wetting agents, emulsifiers and solvents by, 287
Sulfonic acid catalysts, 420
  acids as catalysts, 246
Sulfur, 145
  as bromine carrier, 250
  as chlorine carrier, 250
  as hydrogen carrier, 354
  catalyst poison, 208
  compounds in petroleum, 289
  dichloride, 145
  dioxide as catalyst, 263
  dioxide, nickel poison, 406
  dioxide, oxidation, catalysts for, 191, 192
  dioxide, oxidation of, 7
  dioxide, oxidation of, mechanism, 87
  dioxide, oxidation of, over MnO_2, 291
  dioxide, reduction of, 138
  dioxide, removal from flue gases, 291
  from sulfur dioxide, 138
  nickel poison, 369
  poison for ammonia catalyst, 311
  removal from feed, 369
  resistant catalyst, 362
  trioxide as catalyst, 266
Sulfuric acid, 145
  acid, alkylation catalyst, 253, 254, 259
  acid alkylation process, motor fuels, 377
  acid, as catalyst, 248, 249
  acid, catalyst in hydration of olefin oxide, 346

Sulfuric (*Cont.*):
  acid, concentrated, as alkylating catalyst, 256
  acid condensation catalyst, 267
  acid, dehydration of castor oil, 415
  acid, hydrolysis of oils and fats, 417
  acid, increase of oxidizing power, 189
  acid, polymerization of olefins, 373
  anhydride catalyst, preparation of, 142, 143
Sulfuryl chloride as chlorinating agent, 251
  chloride, sulfonation with, 287
Supports for nickel catalysts, 160
Surface area measurement, 93
  forces of a crystal, 34
  reaction, nitride formation on ammonia catalysts, 309
  reaction, rate of, 34
  reactions, 25
Surfaces, specificity of, 99
Symposium, chlorination processes, 252
  hydrogenation, 219
  synthetic rubber, 390
Synergism, 111
Synthesis of ammonia, 307, 309
Synthetic polymers, hydrogenated to blending agents, 362
  rubber, 384
  rubber emulsion, 395, 396
  rubber latex, 395, 396
  rubbers derived from ethylene, 394
  rubbers from calcium carbide, 392
  rubbers, structure of, 391
  rubbers with benzene and phenol, 393
  solvent, by high-pressure hydrogenation, 147
Synthols, 329

Tablets, catalyst, 147
  chromium oxide, 213
Tallow, hydrolysis of, 418, 419
Tantalum chloride, 257
Tar acids, 357
  high-temperature, hydrogenation of, 259
Tars, hydrogenation of, 353
Tautomerism of α-diketones, 78
Technical composition, 15
Temperature, absorption of hydrocarbons in acid, 283
  and rate constants, hydrolysis of phthalic acid esters, 240
  coefficient, hydrogenation rate of coal, 352
  polymerization, 278
Terephthalic acid diethyl ester, alkaline hydrolysis, 240
Testing of progress of hydrogenation, 406
Tetrachlorethane, 328
Tetradecane, 337
Tetraethyl lead susceptibility, 366
Tetrahydrobenzene, intermediate, 350
Tetrahydronaphthalene as solvent, 351, 354, 355, 357
Thermofor Catalytic Cracking Synthetic Bead Catalyst, 180
Thiamin as growth substance, 14
Thiokol A, 392, 394
Thiokol B, 392, 394
Thiophene, 218
  desulfurization of, 289
Thiophenes in petroleum feeds, 379
Thiourea, desulfurization of, 288
Thoria, 319
  as activator for nickel catalyst, 160
  as dehydration catalyst, 242
  as promoter for nickel catalyst, 51
  catalyst, 292
Thorium, 335
  chloride, 257
  oxide as promoter for tungsten (electron emission), 29
Thyroxin as catalyst, 301
Tin, allotropic change, 123
  chloride, 412
  compounds, 140
  oxalate, 353
  oxide, 412
  sulfide, 353
Titania, 141
Titanium, 323
  chloride, 257
Toluene, chlorination, 250
  from n-heptane, 212
  oxidation, 203
p-Toluene sulfonic acid, dehydration of castor oil, 416
Toluenes from n-heptanes and n-heptenes, 217

Total composition, 16
Trace catalysis, 16
  composition, 15
Trans type fatty acids, 405
Trialkyl phosphates, 254
Tricresyl phosphate, 394
Tridecanes, 337
Triglycerides, hydrolysis of, 238
Trimethyl ethylene, preparation of, 265
Trinitrobenzoic acid, decarboxylation of, 76
Triolein glyceride, hydrogenation of, 396
Triple bonds, hydrogenation of, 222
  hydrogenation, 225, 226
Tripoli, 144
Tripane process, 382
Tung oil substitute, 412
Tungsten filament, catalytic action of, 26
  catalyst, nitride formation on, 102
  oxide, 148
  oxide, yellow, 26
  sulfide, 148, 354
Tungstic acid, dehydration of castor oil, 416
Twitchell agent, 297, 420
Two-component mixtures, hydrogenation of, 112
Two-stage hydrogenation, 359
Tyrosin as catalyst, 301

Ultra-trace composition, 15
Ultraviolet absorption spectra, 20, 22
n-Undecyl cyanide, 244
Universal oil process, 374
Unsaturated alcohols, primary, dehydrogenation of, 208
  compounds, preparation of, 204
Unsaturation, 276, 277
  of castor oil, increase of, 412, 413
Uranium, 310
  carbide, 148
  carbide ammonium catalyst, 308
  oxide, colloidal, 148
  oxides, 148
Urea, hydrolysis by enzymes, 297
Urea-formaldehyde, 273
Urease, 297
Ustilago violacea, growth substance for, 14

Vanadic acid, preparation of, 142
  acid, reduction with alcohol, 174
Vanadium oxide, catalyst, 144
  oxide, oxidation of methyl alcohol, 202
  pentoxide, benzene oxidation, 203
  pentoxide catalyst, 198
  pentoxide, oxidation of toluene or anthracene, 203
  platinum catalyst, 144
Vanadyl hydroxide, 174
Vapor-phase destructive hydrogenation, 353
  esterification, 178, 247
Vegetable and animal oils and fats, catalyst poisons, 402
  fats and oils, hydrocarbons from, 412
  oils, conjugation essays, 263
  oils, decomposition of, 412
  oils, exchange esterification, 247
  oils, exhaustively hydrogenated, 397
  oils, glyceride content, 397
  oils, isomerization of, 263
  oils, polymerization of, 279
  oils, selective hydrogenation, 403, 404
  oils, technical hydrogenation, 397, 398
Velocity constants, ester hydrolysis, 239
  of chemical reactions, equation, 47
  of hydrogenation, factors in, 101
  of hydrogenation, maximum, 224
Vinyl acetate from acetic acid and acetylene, 326
  acetylene, formation of, 386
  benzene, 391
  chloride, 391, 394
  chloride—vinyl acetate polymerization, 284
  ether, hydrolysis constant, 241
Violet acid, 192
Vistanex, 391
Vitamins, 15
  function in plants, 112
Volumes, true, constant size, 122
  true, of alkalies, 122

Wachter's rule, 282
Wall catalysis, 308, 353
  catalysts, alkali halides, 109

Wall (*Cont.*):
  deposits, catalytic action of, 109
  reaction, 63, 64, 65, 107
Walls of converters, catalytic effect, 109
Water as autocatalyst, 41
  as catalyst, 248
  as inhibitor, 266
  catalytic action, 209
  catalytic mechanism, 211
  distilled, purity of, 16
  formation, catalysts for, 104
  formation, 8th group of metals as catalysts, mechanism, 118
  gas, 311, 332
  gas, catalysis mechanism, 331
  gas, composition of, 312
  gas, conversion at atmospheric pressure, 331
  gas conversion, copper-vanadyl catalyst, 175
  gas conversion, nickel catalyst for, 160
  gas, conversion of, under high pressure, 330
  gas, conversion operation conditions, 332
  gas, from natural gas, 338
  poison action of, 213
  scrubbing, CO_2, 364
  small quantities, as negative catalyst, 36
  vapor as catalyst poison in ammonia synthesis, 58
  vapor, catalyst in powder reactions, 110
Wax from Kogasin synthesis, 336
  from water gas, 334
  penetration of Kogasin catalysts, 336
Waxes, Fischer-Tropsch synthesis, 337
  hydrogenation of oleic acid, 411
Waxy esters from glycerides, 411
Weathering processes, 2
Wetting agents, formation of, 287
Wetting-out agents, 412
Whale oil, hydrogenation of, 404
Wieland's oxidation theory, 186
Wine-making, 295
Wood charcoal, hydrogenation of, 357
  pulping, with butyl alcohol, 247
  tar, hydrogenation of, 360
World capacity, ammonia production, 315

Xanthic acid, decomposition of, 76
Xylenes, chlorination, 250
  from n-octanes and n-octenes, 217

Zeolites, synthetic, 174, 322
Zinc, as paint drier, 135
  catalyst, dehydrogenation, 211
  impurities in, 17
Zinc chloride, 134, 249, 412
  as condensation catalyst, 267
  as dehydration catalyst, 242
Zinc chromite, esters and alcohols from oils, 410
Zinc—chromium oxide, 147, 341, 342
Zinc fluoride as fluorine carrier, 250
Zinc oxide, 134, 341, 412
  decomposition of methyl alcohol, 342
  hydration catalyst, 347
  reduction of, 134
Zirconia, 141
Zirconia on alumina, 321
Zirconium chloride, 257

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